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No. 1025

SELF-IGNITION AND COMBUSTION OF GASES

By A. S. Sokolik

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SELF-IGNITION AND COMBUSTION OF GASES*

By A. S. Sokolik

The extraordinary diversity of the combustion phenomena and their significance for the most important fields of engineering application have given rise to a large number of investigations both experimental and theoretical the object of which is to give a chemicophysical description of the various types of combustion. The most urgent as well as the most complicated problem is that of finding the relation between the various combustion processes (for example, self-ignition, flame propagation, detonation) and the kinetics of the chemical processes involved (complex chains of oxidizing reactions) that lie at the basis of every phenomenon of combustion and inflammation. Only the first steps have been taken in this direction, limited for the most part to a mere statement of the problem to be investigated and an indication of the methods of investigation to be followed, but we are still far from any theoretical generalizations which would enable us, at least for the simplest cases, to determine by computation the temperature, limiting pressure, or self-ignition lag, velocity of flame propagation, detonation limits, etc., for any given physicochemical conditions.

The setting up of a general theory of combustion is rendered difficult by the complexity of the phenomenon, associated with the simultaneous effects of purely physico-chemical factors (heat generation and hydrodynamics), and the mechanism of the preignition processes and kinetics of the reaction.

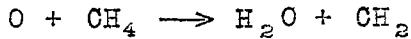
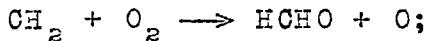
Notwithstanding the progress made in the development of these fields of physical chemistry especially in the working out of a general theory of chain reactions, we are still constrained to make use of more or less hypothetical schemes even when considering the very simplest chemical systems, such as $H_2 + O_2$ or $CH_4 + O_2$. As an example, let us consider one of the schemes giving the successive elementary reactions in the combustion of methane, as proposed by Semenoff (reference 1) and Norrish (reference 2).

*Progr. Phys. Sci. (USSR) 23, no. 3, 1940, pp. 209-250.

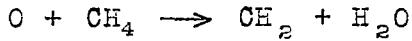
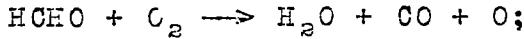
According to this scheme the chain reaction is begun by the reaction of a molecule of CH_4 with atomic oxygen (which thus presupposes a preliminary dissociation of the oxygen molecule into atoms):



The chain is then extended through the radicals CH_2 and atomic oxygen O:



Besides this fundamental chain there is possible the formation of new chains (that is, branching chains), for example, as a result of the oxidation of formaldehyde:



We may note the fact that this scheme figure, together with others, only as one of the many possible reaction mechanisms and, what is more important that the separate stages of this scheme have not been confirmed by any direct experiment, but have received only a number of incidental indirect experimental proofs, as, for example, the establishment of the existence of the free radical CH_2 (reference 3).

Thus our present-day conceptions as to the concrete mechanism of the ignition reactions are in no case based on indisputable experimental data and appear only as probable hypothetical schemes.

The most important problems of investigation are therefore the chemical nature of the combustion reactions and the explanation of those laws which connect combustion with the general kinetic character of combustible mixtures.

In our present article we exclude from consideration investigations of a purely chemical nature notwithstanding their undoubted importance both for the theory of combustion and for certain technical problems (especially for problems of detonation in the internal combustion engine). Our paper is therefore devoted essentially to those investigations of recent years in which new combustion phenomena

or new methods of studying them experimentally are brought out or to investigations that throw new light on already known phenomena.

SELF-IGNITION OF GASEOUS MIXTURES

The gradual increase in the temperature of a combustible mixture at constant pressure or increase in the pressure at constant temperature leads to an acceleration in the velocity of reaction until the rate of heat liberation starts to exceed the rate of heat conduction to the walls of the vessel. As a result, there is a progressive self-heating of the combustible mixture that leads to a still greater spontaneous increase in the velocity of the reaction and practically instantaneous development of heat of reaction within a certain volume of the gas; that is, to its inflammation.

The above conception of the limiting conditions of self-ignition was expressed by Van't Hoff (reference 4) in the following words: "The temperature of self-ignition is that temperature at which the initial loss of heat caused by heat conduction, and so forth, is equal to the heat which at that instant is produced by the chemical change." In accordance with this conception, the explosion itself should be preceded by a period of relatively slow increase in the velocity of the chemical reaction corresponding to the slow rise in the temperature, at times hardly noticeable. This interval (called the induction period or the self-ignition lag) can be visually observed, for example, on the admission of a combustible mixture into a bomb provided at one end with a window. Under certain conditions, as for the mixture of methane or ethane with air at temperatures of about 500° C, explosion can occur only after an interval of several minutes after admission of the mixture into the heated bomb. This means that for self-ignition to occur it is not sufficient merely that the mixture be heated up to a certain temperature beyond the limiting temperature but a definite time interval is necessary for the development of the preinflammation reaction corresponding to the induction period. For many practical cases the possibility of explosion itself is conditioned by the time factor.

Let us consider the question of the application of electric safety lamps in an atmosphere containing combustible gases, for example, in coal mines where the presence of

methane is possible, or in naphtha tankers where the atmosphere may contain the vapors of various hydrocarbons entering into the composition of naphtha and its products (pentane, etc.). In the case of accidental breaking of the glass bulb of the lamp in such an atmosphere an explosion is possible from contact of the gas with the glowing filament heated to a temperature of about 3000° C; that is, much higher than the minimum self-ignition temperature of any combustible mixture (for methane it is less than 500° - 450° C). To prevent explosion, such lamps are provided with special automatic cutouts that disconnect the circuit at the instant the protective covering surrounding the electric lamp and filled with inert gas under pressure is broken. Immediately after disconnection of the circuit the hot filament and the combustible mixture coming in contact with it partly diluted with the inert gas start to cool, the rate of cooling depending on the filament temperature. As measurements have shown, however, this temperature of the filament at the instant of contact with the combustible mixture is considerably higher than the minimum self-ignition temperature. Hence the possibility of preventing explosion will depend primarily on the length of the induction period corresponding to the given temperature conditions. In the case of methane or pentane, which, as experiment has shown, self-ignite with a relatively long delay period (of several seconds), it is possible to design an efficient safety lamp. These lamps are found, however, to be quite unsafe in an atmosphere containing hydrogen (in potassium mines, for example) in correspondence with the fact that for this gas the self-ignition lag is exceedingly short (of the order of 0.01 sec) although the minimum self-ignition temperature differs little from that of pentane (also about 500° C).

The existence of the self-ignition lag shows up in the fact that self-ignition under no experimental conditions occurs simultaneously throughout a sufficiently large volume of gas heated to the self-ignition temperature. If, for example, the combustible mixture is heated to the self-ignition temperature by adiabatic compression, then, as observed by Dickson (reference 5) who photographed the process of the flame development on a film moving in a direction perpendicular to the axis of the bomb), self-ignition occurs always at some point. This fact is a result of the unavoidable non-uniformity of the temperature distribution and especially of the active centers, so that at any relatively small part of the volume with maximum temperature and concentration of active molecules the

conditions exist for an earlier completion of the induction period.* The local occurrence of inflammation, as shown by the flame photographs of figure 1, is propagated over the rest of the volume of the gas almost in the same manner as the ignition of a cold gas by an electric spark.

FUNDAMENTAL LAWS OF SELF-IGNITION

As follows from the definition of self-ignition, the latter is determined by the condition where the increase in the temperature at constant pressure gives a rate of increase in the velocity of the reaction and liberation of heat

(according to the law of Arrhenius: $w \sim Q_a = Ae^{-\frac{E}{RT}}$),

considerably greater than the loss in heat from heat transfer, which may be taken as proportional to the difference in temperature between the gas and the surrounding medium ($Q_b = k(T - T_0)$). In exactly the same manner the reaction velocity and heat liberation increase with rise in pressure at constant temperature when the heat lost by transfer in general does not change with the pressure and the reaction velocity is proportional to a certain power of the pressure (for example, $w \sim ap^2$ for a bimolecular reaction). From this it evidently follows that it is incorrect to consider the self-ignition temperature as a physical constant for a given mixture but that its value may within wide limits vary with the conditions under which the heat is liberated (diameter of the vessel, character of heat transfer to the walls of the vessel, etc.).

On the basis of the above considerations Semenoff was the first to give a mathematical formulation for the limiting condition of self-ignition, namely, as the condition of equality of heat loss and heat gain from the reaction. Graphically this corresponds to the condition of tangency of one of the curves (2 in fig. 2) showing the variation with temperature of the amount of heat liberated per second

($-\frac{E}{RT}$) at various pressures according to the law $Q_a = Ae^{-\frac{E}{RT}}$ and the straight line of heat lost by heat transfer as a function of the gas temperature for constant temperature of the bomb T_0 (corresponding to the law $Q_b = k(T - T_0)$). The pressure

*On the manner of formation of these temperature fluctuations in the gas, see Semenoff (loc. cit. 114) and Norrish (reference 6).

to which curve 2 tangent to the straight line corresponds is the critical minimum pressure at which self-ignition is possible for the given temperature of the bomb. The condition of tangency gives the following relation between the critical pressure and the self-ignition temperature:

$$\left(\frac{p}{T_0}\right)^n e^{-\frac{E}{RT_0}} = \text{const}$$

$$\text{or } \lg \frac{p}{T_0} = \frac{A}{T_0} + B \quad \text{where } A = \frac{E \lg e}{nR} \quad \text{and } B \text{ is a constant}$$

depending on the composition of the mixture and on the physical conditions of the explosion (in particular, on the conditions of heat liberation, for example, the diameter of the vessel).

The formula of Semenoff not only gives the relation between the values of the critical pressure and temperature of self-ignition but their dependence on the kinetic properties of the mixture as determined by the energies of activation (constant A) and the physical conditions of the explosion (constant B) and thus the method is indicated ~~of~~ computing the self-ignition limits.

On the basis of the work of Semenoff a more rigorous theory of thermal explosion was then developed in the papers of Todes (reference 7) and Frank-Kamenetsky (reference 8) which showed the possibility of computing the self-ignition temperature and pressure under definite conditions of heat liberation for very simple types of reaction (for example, the explosive decomposition of N_2O (reference 9)).

The formula of Semenoff has been frequently confirmed experimentally, at first by Zagulin (reference 10) and later by a number of other investigators under conditions of explosion at low pressures (of the order of several centimeters Hg). Under these conditions there was always observed a lowering of the critical self-ignition temperature in exact correspondence with the formula.

A further extension of the field of experiment to self-ignition at higher pressures (especially important for hydrocarbon-air mixtures and applicable to problems of the internal combustion engine) has brought out the limit of applicability of Semenoff's formula.* This is clearly shown

*See the corresponding remarks in the papers of Naylor and Wheeler (reference 11) and our own (reference 16).

by the appearance of the limiting curve of the self-ignition region in figure 3, typical for the majority of hydrocarbons. Only a small portion, corresponding to low pressures and high temperatures (AB in fig. 3), gives such a lowering in the critical pressure with rise in self-ignition temperature as required by Semenoff's formula. For the remaining larger portion of the limiting curve experiment gives another relation between these explosion parameters, for example, an increase in P_{expl} with increase in T on the portion BC corresponding to the upper limit of self-ignition (where the self-ignition vanishes with increasing pressure at constant temperature) or almost a complete constancy of the critical pressure with change in temperature within wide limits - from 400° to 450° to 300° C on the portion DE, corresponding to the transition from the upper temperature zone to the lower temperature zone of self-ignition;* or vice-versa an almost complete constancy of self-ignition temperature with change in pressure within wide limits (from 2 to 30 to 40 atm) on the portion EF corresponding to the minimum self-ignition temperature temperature.

Without considering in detail the cause which gives rise to the different variation of the two explosion parameters, namely, the temperature and pressure of self-ignition, we may observe merely that this in no way conflicts with the correctness of the considerations upon which the formula of Semenoff is based but is associated either with the special effect of the pressure on the development of chain reactions (for example, with the increased breaking of the reaction chains and the increased difficulty of self-ignition due to the increased number of triple impacts with pressure rise) or with the fact that the preinflammation reactions in the low-temperature zone consist of several opposing processes reacting differently on the variations of the temperature and pressure. Independently, however, of these reasons the conclusion is indisputable, namely, that the self-ignition temperature not only is not a physicochemical constant for a given combustible mixture (since it depends very largely on a number of physical conditions determining the character of the heat liberation of the reacting gas), but the very concept of self-ignition temperature has no physical significance if the corresponding pressure is not simultaneously indicated.

*According to the tests of Townend (reference 12) on this portion of the curve there is even a sharp drop in P_{expl} with decrease in temperature a fact associated with circumstances of his experimental procedure (reference 13).

In exactly the same manner the self-ignition temperature and pressure are closely bound up with the time factor, namely, the corresponding induction period. The quantitative relation between the induction period and the self-ignition temperature was first given by Tizard and Pye (reference 14) in their fundamental self-ignition investigations at adiabatic compression. Subsequently a more general formula was derived by Semenoff giving the relation between all three explosion parameters—pressure (p), temperature (T), and induction period (τ). The formula followed from the general law of the development of the reaction velocity with time: $w = ae^{\varphi t}$ and the general condition for self-ignition $\varphi\tau = \text{const}$, where

$$\varphi = p^{n_e} - \frac{\gamma}{T}$$

$$-\frac{\gamma}{T}$$

The general formula $\tau p^{n_e} = \text{const}$ was first experimentally established by Neiman and Yegorov (reference 15) for the self-ignition of methane at low pressures. As follows from the formula, the induction period should decrease with increasing pressure and rise in temperature. The effect of the latter is especially large for a sufficiently large value of the temperature coefficient γ . Thus for $\gamma = 20,000$ (and in certain cases its value is still higher) an increase in the temperature of 10° at 300° C almost halves the ignition lag.

The same relation between the ignition lag and the temperature may be considered also from a different point of view, namely, self-ignition should occur at a lower temperature (but not below the minimal) the greater the time allowed for the development of the preinflammation reaction.

The extension of the field of experiment to higher pressures also showed, however, the limited applicability of this formula in its general form, for example, the constancy of the lag for hydrocarbon-air mixtures in the temperature range 400° to 600° C , and conversely, the constancy of the lag with pressure in the low-temperature range 400° to 280° C (reference 16). Investigation at high self-ignition pressures of hydrogen-air mixtures showed that for these the induction period does not depend on the temperature and sharply decreases with rise in pressure over the entire temperature interval: 500° to 700° C . Thus the self-ignition of hydrogen-air mixtures

at $p > 1$ to 1.5 atm is described by the formula: $\tau p^3 = \text{const}$ independent of the temperature at which the self-ignition occurs (reference 16). In the original papers are given examples of the use of these experimental results for the practical treatment of important explosion phenomena.

On the basis of the fact that the self-ignition temperature is not a chemophysical constant there has been observed a tendency among a number of recent investigators to exclude, in general, all explosion parameters (T, p, τ) taken from physical chemistry and substitute for them basic magnitudes which directly characterize the kinetics of the process, for example, the reaction velocity, its energy of activation, etc. This tendency is somewhat justified by the difficulty of constructing a strict theory of flame propagation making use of the explosion parameters. Their experimental values and, in particular, the relations experimentally established between them provide, however, a correct orientation for the consideration of many technical problems. If, for example, the absolute values of the induction periods, measured on air mixtures of hydrogen or pentane under definite laboratory conditions cannot be applied to actual explosion conditions (for example, explosion from a heated lamp filament) these values of the induction periods nevertheless provide a desired criterion for judging the relative safety of the apparatus in an atmosphere of pentane and hydrogen.

The comparison study of the induction periods of heavy Diesel oils in a bomb under conditions, in general, different from those in the Diesel engine nevertheless makes possible a correct estimate of the characteristics defined by the so-called "cetene number" (references 17 to 19).

The bomb investigation of the relation between the self-signition lag of light engine fuels and the pressure and temperature in various temperature intervals has led not only to a number of important conclusions on the conditions under which detonation occurs in the spark-ignition engine but also to a correct quantitative relation between the value of the temperature coefficient γ for the induction period and the critical degree of compression characteristic of the detonation properties of the engine fuels. (See reference 20)

INVESTIGATIONS ON SHORT INDUCTION PERIODS

Method of rapid admission.— The visual measurement of ignition lags is possible only under restricted conditions either low pressures or low temperatures (near the minimum temperature) for lags not less than 2 to 3 seconds. Of greatest practical interest, however, is the study of short ignition lags. In the work of our laboratories (the first systematic investigations of self-ignition with short lags) there was successfully used the method of quick admission, schematically shown in figure 4.

The combustible mixture from the vessel 1 is admitted to the heated bomb 2 through a quick-acting spring-loaded nozzle 3 so that the entire filling process of the bomb takes place in $3 \text{ to } 5 \times 10^{-2}$ second. The rapidity of the admission, the fundamental characteristic of the method, is required for the study of short induction periods. The induction period is measured with the aid of an optical diaphragm of manometer 5 by photographically recording the pressures. A sample recording is shown in figure 5. The induction period here corresponds to the horizontal part of the pressure diagram from the instant of completion of admission to the sharp rise of pressure on explosion.

In addition, however, to determining the induction period a detailed investigation of the pre-explosion processes in the gas is very important. This is a problem of great practical difficulty since it is sometimes necessary to measure the extremely small pressure variations due to the slow reactions during the induction period while simultaneously recording explosion pressures of the order of tens of atmospheres. The difficulty is, however, entirely eliminated by the use of an optical differential manometer applied by Neiman and his coworkers (reference 21), Kane (reference 22) and in its most perfected form in our laboratories (fig. 6).

The manometer is divided by a thin diaphragm 1 into two chambers, one of which communicates with the vessel 4 and the other with the bomb 6. The vessel 4 is provided with an electromagnetically operated nozzle that closes the admission passage by the action of a spring and opens when the circuit through coil 5 is closed. The thin diaphragm of the manometer is connected with an optical system and is stopped on both sides by the thick perforated membranes 2 and 3. When the vessel 4 is filled to the

given pressure (10 to 15 atm) the thin diaphragm presses against the stop and is deflected in correspondence with the increase in pressure on filling the vessel.

This pressure is recorded on the film as line a-b, figure 7. When the mixture is admitted to the initially pumped-out bomb the pressures in the two chambers of the manometer balance and stop 2 together with the diaphragm return to the initial position. The process of balancing the pressures in vessels 4 and 6, that is, the admission process, is recorded on the film as line b-c, making it possible to control the admission rate which, as shown by experiment, is particularly important for the stabilization of the self-ignition conditions (reference 13). On the diagram there is furthermore fixed the instant of disconnection of the electromagnet d. The bomb now communicates with only one chamber of the manometer. The pressure increase (e-f) from the reaction is recorded at first only by the thin diaphragm 1 and then starting with pressures higher than 100 millimeters up to the explosion pressure by the simultaneous deflection of the thin diaphragm and the thick one 3. At the initial pressures (5 to 10 atm) our differential manometer records change in pressure down to 5 millimeters and explosion pressures.

The photo record of figure 7 was taken under conditions of low-temperature self-ignition of a mixture of pentane and air. We are dealing here with a two-stage self-ignition process, first studied by Townend (reference 12), Neiman (reference 21), and Kane (reference 22). The explosion itself in this case is preceded by the formation of a cold flame giving the products of the incomplete oxidation of the hydrocarbon.

The sensitive diaphragm of the differential manometer shows no noticeable increase in the pressure (and probably the temperature) during the induction period τ_1 up to the moment of the occurrence of the cold flame. We are therefore dealing here with an isothermal process in which the development of the preinflammation reaction is determined exclusively by the branching of reaction chains. An increase of the pressure in the cold flame characterizes its intensity and the degree of oxidation of the hydrocarbon.

After the cold flame and induction period τ_2 thermal explosion occurs at a relatively higher temperature with the formation of the products of complete combustion CO_2 and H_2O .

The study of both stages of the explosion process by these methods together with the chemical analysis appears very promising not only for learning the mechanism of self-ignition but also for throwing light on the urgent technical problems connected with the kinetic characteristics of antidetonating fuels.

Method of flow through a tube.— If the combustible mixture is admitted through a tube heated to a certain temperature then at a sufficiently high velocity of the flow the self-ignition vanishes, the time in which the gas is in the tube being less than the induction period corresponding to the given temperature. The necessity, however, of applying high velocities renders this method difficult for the study of short ignition lags.

An attempt to get around this difficulty was made by Sachsse (reference 23) by establishing along the tube the temperature distribution shown in figure 8. The passage of the gas through the cross sections of the tube with gradual increase of the temperature from 100° to 820° C is considered by the author as a process of warming up and only the time of passing through the small portion with the maximum temperature (820° to 850° C) serves in his tests as a measure of the induction period corresponding to this temperature.

The limitation of this method of measuring the induction period is obvious since the time of preliminary preheating of the mixture (during which chemical changes are unavoidable) is six times as large as the time interval during which the mixture is at the maximum temperature.

Thus the condition is neglected which is put at the basis of our method, that is, that in measuring short induction periods the time of preliminary preheating should be less than the minimum value of the induction period (or comparable with it).

Measurements by the method of Sachsse will therefore lead to an impairment in the results which will be the greater the more the mixture reacts during the preheating. For methane, for which appreciable reaction velocities are possible only at relatively high temperature (near the maximum temperature of the tube) this method may give a value of the induction period relatively near the true value. For higher hydrocarbons, however, that start to oxidize at considerably lower temperature the method of Sachsse will

give results known to be incorrect, for example, to the maximum temperature there will arbitrarily correspond temperature coefficients that belong with the lower temperatures of the preliminary heating.

Method of heated particles.— One of the possibilities of explosion of a mine gas is by ignition from heated particles from various sources, for example, friction sparks (from certain rock-cutting machines). The investigation of the self-ignition of combustible gas mixtures due to heated particles carried through the gas at definite velocities besides being of practical interest provides a method of studying self-ignition for the case of very short ignition lags.

The scheme of such a method as employed by Silver (reference 24) is shown in figure 9. The small sphere (of quartz or platinum) is heated in a quartz tube PP to a certain temperature measured by an optical pyrometer. By compressed air the sphere is projected out from the tube and passes at a certain velocity into a brass box filled with the combustible mixture to be tested. The valve for the admission of air into the tube PP is opened by the freeing of a clutch (schematically represented by TS) while simultaneously the electric circuit is closed in the solenoid. The iron core L then lifts the plate S so that the slot Sl makes PP communicate with the box. The latter is provided with the screen T that reflects the sphere and with a cellophane diaphragm CR the rupture of which serves to indicate the self-ignition of the gas. Approximately the same apparatus was used in more recent tests of the same laboratory (Glasgow University) by Paterson (reference 25) with the added provision of measuring the velocity of the sphere with the aid of a ballistic pendulum and with a device for preventing the compressed air from entering the explosion vessel together with the sphere.

At relatively constant velocity of the sphere (2 to 5 m/sec) Silver measured the limiting temperature at which inflammation of the mixtures of air with pentane, illuminating gas, and hydrogen was possible immediately after the sphere reached the explosion vessel. The method of Silver thus essentially provides a measure of the self-ignition temperature of a gas from heated surfaces for constant ignition lags near zero. Under these conditions, as seen on figure 10, the self-ignition of the gases occurs at lower temperatures the larger the diameter of the heated sphere. Particularly large for such ignition lag is the self-ignition temperature of methane for which self-ignition

could be obtained only with a sphere of diameter of 6.5 millimeters at a temperature of about 1200° C.

Silver considers the self-ignition process of the gaseous envelope surrounding the heated sphere from the point of view of the thermal theory. For a layer of gas of thickness dr surrounding a sphere of diameter $a = 2r$, the condition for self-ignition will be given by the equality of the heat loss in the surrounding medium at temperature T_0 and the heat liberated in the same layer of the gas by the reaction. The heat losses are computed as the difference between the heat conducted through the surface of the layer in the surrounding gas and the heat entering the layer from the sphere, $8\pi a\rho(T_p - T_0)dr$ where ρ is the heat transfer coefficient.

The heat given off by the reaction in this layer is

$$-\frac{A}{RT}$$

equal to $4\pi a^2 dr Q \beta e^{-\frac{A}{RT}}$ where β is a constant including the exponential factor in the equation of Arrhenius. Thus the heat gain increases more rapidly with increase in the diameter of the sphere (proportional to a^2) than the heat loss (proportional to a), which fact also explains the facilitating of self-ignition with increase in the sphere diameter.

The self-ignition condition is obtained by Silver as the equation

$$8\pi a\rho(T_p - T_0)dr = 4\pi a^2 dr Q \beta e^{-\frac{A}{RT}}$$

which may be brought to the form

$$a = \frac{2\rho}{\beta Q} (T_p - T_0) e^{\frac{A}{RT}}$$

or

$$\lg \frac{T_p - T_0}{a} = \lg \frac{\beta Q}{2\rho} - \frac{A}{RT}$$

This equation well describes the experimental results shown in figure 10 but with somewhat unusual consequences.

The values of $\lg \frac{T_p - T_0}{a}$ plotted against $\frac{1}{T_p}$ give as

follows from the equation, a straight line. For all gases investigated, however, Silver obtains the same slope for the lines, that is, the same value of the activation energy, from 20.5 to 22.5 calories. In the opinion of Silver this means that under the given conditions the self-ignition of the gas is the result of a heterogeneous reaction on the surface of the sphere although this explanation little agrees with the identical results obtained by him for quartz and platinum spheres.

Paterson investigated the effect of the velocity of the particles on the self-ignition temperature of illuminating gas, an increase in the temperature with increasing velocity of the particles being taken by Paterson as proof of the fact that the self-ignition process must not be considered from the point of view of the "surface theory" only and that a considerable part is here played by the "mechanism of the energy transfer, whether thermal or by a chain process." The character of the surface, however, (conditioned, for example, by previous use of the spheres for explosion tests) is also of fundamental importance.

Analyzing the self-ignition process as Silver does from the point of view of the thermal theory Paterson considers the heat transfer as mainly convective. Hence in the formula for the heat transfer

$$\frac{dH_C}{dt} = A a \mu c_p (T_s - T_\infty) \sqrt{Re}$$

where the Reynolds number $Re = 2Vap/\mu$ the velocity enters so that the heat is proportional to \sqrt{V} . Paterson obtains a relation of the form

$$D(T_s - T_\infty) V^{1/2} = \beta a^{3/2} e^{-\frac{A}{RT_s}}$$

where D is a constant that includes the density, viscosity, and heat of the reaction.

As may be seen, the relation obtained by Paterson between the self-ignition temperature and the velocity of the particles in no way indicates any variation with the temperature of the self-ignition lag, which in this case, as also in the tests of Silver, remains constant and near the value zero. An increase, however, in the self-ignition temperature

with increase in the velocity of the particles, as follows from the given formula, is directly associated with an increase in the heat loss from convection proportional to \sqrt{V} .

The equation of Paterson, presupposes moreover a lowering in the self-ignition temperature at constant velocity (V) and diameter of particle (d) with rise in the temperature of the gas (T_m). As has been shown by tests, however, a rise in the initial temperature even by 200°C in no way showed any effect upon the magnitude of the minimum temperature of the particle.

The tests of Silver and Paterson do not provide any direct experimental data as to the dependence of short ignition lags on the temperature and consequently cannot be used for checking the nondependence of short ignition lags on the temperature as found in our tests. Some results of the works considered, however, especially the nondependence of the temperature coefficient on the properties of the reacting gas, undoubtedly indicate a specific character of the self-ignition under conditions of short lags and lend special interest toward further investigation in this direction.

FLAME PROPAGATION

Normal combustion.— Nondetonating combustion presents a complicated phenomenon in which the motion of the gas itself is unavoidably included along with the propagation of the reaction zones with respect to the gas. This complication lies in the very nature of "slow" burning in that the velocity of propagation of the reaction zone with respect to the gas (a process conditioned by heat conduction and diffusion) is considerably less than the velocity of propagation of the compression waves which are formed in the process of inflammation of each layer of gas and its subsequent propagation.

The propagation of these disturbances in the gas occurs with the velocity of sound; whereas the velocity of propagation of the reaction zone rarely exceeds a few meters per second. This unavoidable separation of the mechanical effect of combustion from the combustion zone itself produces a mass flow of the gas ahead of the flame front. The propagation of the reaction zone thus occurs in a moving gas and it is necessary to take account not only of the motion of the gas along the axis of the tube (the velocity of which

is simply added to the velocity of propagation of the reaction zone with respect to the stationary gas) but also of disordered turbulent motions that increase the heat transmission from the combustion zone to the fresh gas.

The turbulence formed ahead of the flame front in "slow" combustion is a fundamental factor in causing explosions by coal mine dust. The ignition of mine gas (methane) would in itself present no serious danger in view of the relatively small quantities if it were not a principal cause of the explosion of coal dust. The air motions themselves ahead of the flame front raise the coal dust from the ground mixing the dust with air and thus form a medium in which the explosion is propagated with continually increasing velocity (sometimes above 1000 m/sec) and develop considerable pressure (higher than 10 atm). The formation of a dust cloud ahead of the flame front is seen on the photograph of figure 11 taken at a certain time before the appearance of flames at the mouth of an experimental mine.

The investigation of the air motions ahead of the flame front is one of the most important problems carried out in adits under conditions accurately reproducing those of mine explosions,* and among the various means taken for the prevention of explosions not the least important are those the object of which is to make difficult the formation of dust clouds.

The investigations of Coward (reference 26) of recent years have brought out still another important factor on which the velocity of flame propagation depends: namely, the change in the flame front itself under the effect of "convection flows caused by differences in the densities of the burning and the fresh gas." Successive photographs of a flame front, obtained by Coward in various stages of propagation along the tube, show that a plane wave front, or as is often assumed, a hemispherical front is in most cases an arbitrary idealization. The flame front, as seen in the photographs of figure 12, curves continuously and elongates as it is being propagated so that its surface area is considerably above the cross-sectional area of the tube.

*For a description of these experimental methods see the book of Dolgov and Levitsky, Explosive Properties of Coal Dust. Charkov, 1933.

Starting from the fact that the volume of gas burning per unit of time is proportional to the area of the flame front, Coward introduces the concept of "fundamental velocity" of flame propagation (equivalent to the previously used term "normal velocity") as "the linear velocity of propagation directed perpendicular to the flame front and occurring in a stationary mixture at constant temperature and pressure ahead of the flame front." The observed velocity of the flame propagation corresponding to this will exceed the "fundamental velocity" in proportion to the increase in the flame front area as a result of curvature.

The measurements carried out by Coward and Hartwell for a mixture of methane and air showed that in a tube of diameter 5 centimeters (that is, cross-sectional area of 20 square centimeters) the flame front area varies within the range of 60 to 117 square centimeters for various concentrations of methane. Correspondingly, the velocity of flame propagation changes from 30 to 90 centimeters per second; while the fundamental velocity lies within the range of 6 to 27 centimeters per second.

A particularly strong increase in the flame-front area shows up in tubes of larger diameter where the corresponding flame propagation velocities may be very high. This fact, in particular, must be taken into account in computing safety structures in ventilating systems which handle burning gases.

Measurement of the normal flame velocity.— Only the "fundamental" or "normal" velocity of the flame is directly connected with the physicochemical properties of the combustible mixture and does not depend on those hydrodynamic conditions under which the flame propagation is observed. The "fundamental" velocity thus acquires the significance of a certain physicochemical constant.

Coward and Payman (reference 27) give the following formula that takes account of the basic factors* that determine the velocity of flame propagation: the observed flame velocity = fundamental velocity \times area of flame front/area of tube cross section + velocity of motion of burning medium.

*We say "basic" because here, as in our previous considerations, no account is taken of the change in the gas pressure and temperature which occur in combustion in closed vessels and lead to a continuous change in "fundamental" velocity.

The measurement of the fundamental velocity corresponding to this formula under conditions of combustion in a tube is extremely complicated, not only because of the necessity of measuring the area of a moving flame front (as is shown in fig. 12) but also because of the difficulty of determining the velocity of motion of the gas. As Coward himself remarks, the method indicated is applicable only to such slow-burning mixtures like those of methane and air near the limits of propagation, that is, where the speed of combustion is relatively small and where, consequently, it is permissible to neglect the mass flow of the gas due to the combustion.

However limited the application may be, the indisputable service rendered by Coward is that he revealed a new source of error in the measurement of flame propagation by the classical method of Mallard and Le Chatelier (reference 28). In many investigations of flame propagation in a tube since the time of Le Chatelier, although special precautions were taken that the combustion should take place under conditions of constant pressure (by making the ignition end of the tube communicate with the atmosphere or with a constant pressure reservoir (references 29 and 30)), no attention was paid to the possibility of a change in the flame-propagation velocity due to an increase in the flame-front area. Only the tests of Coward have shown the fundamental possibility in the complicated phenomenon of flame propagation in the tube of separating that part of combustion velocity which has a fundamental physico-chemical significance. A notable confirmation of the correctness of the method of Coward is the agreement of the value of the normal velocity of flame propagation obtained by measurements in tubes with the values for the same mixtures measured in the cone of a Bunsen flame (reference 31).

The normal flame velocity is measured most simply in the flame cone formed by the Bunsen burner. The method of measuring the flame velocity was worked out independently by Gouy (reference 32) and Michelson (reference 33) based on the fact that in the stationary cone of the flame, the surface of which is also that of the combustion front, (or as denoted by Michelson the "inflammation surface") the volume of gas per second flowing out from the burner should be equal to the product of the area of the cone by the value of the normal velocity of propagation. Thus it is also necessary, in order to determine the normal velocity, to measure the area of the flame front. This measurement, however, is a much more simple process, as the flame front is stationary.*

*The theoretical and experimental treatment of this method is given by Chitrin (reference 31) and Smith (reference 34).

The series of photographs obtained by Chitrin, given in figure 13, shows how, for a constant velocity of flow of the gas, the surface of the cone decreases with increase in the flame propagation velocity corresponding to the formula $Q = uS$, where u is the normal velocity of flame propagation and S the area of the cone.

At very large velocities of flame propagation (for example, in the case of the combustion of hydrogen or acetylene), it is necessary to increase correspondingly the velocity of flow of the gas from the burner in order to obtain a flame cone of sufficient height or avoid escape of the flame into the burner.

The possibility of investigation of flame propagation in the burner is also limited, however, by the flow of "secondary" air from the surrounding atmosphere toward the flame. It is due to this unavoidable dilution of the mixture flowing from the burner by the surrounding air that makes it possible to observe in the burner a steady combustion of the mixture with excess of the combustible far beyond the upper limit of inflammation, for example, of mixtures containing up to 17 percent methane (upper explosion limit of methane in air about 13.5 percent). On the other hand, owing to the same dilution with "secondary" air in the burner, combustion is impossible for mixtures with such excess of air for which steady combustion in a tube is still possible, that is, for mixtures lying considerably above the lower limit of inflammation, for example, mixtures containing less than 7.3 percent methane (lower explosion limit of methane in air 5.9 percent).

While the diffusion of air into the flame of a Bunsen burner is of only secondary importance, however, and somewhat changes the composition of the burning mixture, in some cases (match flames, candles, gas lighters) we are dealing with diffusion flames in which the formation of the burning mixture is entirely due to diffusion.*

Among the original methods for studying flame propagation, an interesting one is that of the "constant-pressure bomb" developed in 1926 by Stevens (reference 36) and later perfected by Fiock (reference 37) and others (at the Bureau of Standards, USA).

*The theoretical analysis of diffusion flames is treated in the book of Lewis and Elbe (reference 35)(chapter XIII).

The vessel containing the combustible mixture is in this case a soap bubble at the center of which is located a spark gap (fig. 14). Depending on the pressure at which the flame velocity is measured the bomb in which the soap bubble is placed is filled with an inert gas up to a certain given pressure (above or below atmospheric). Under these conditions the propagation of the flame occurs with a constant increase in volume, as shown by the series of photographs on figure 15, and consequently at constant pressure. The velocity of propagation of the spherical flame front can be measured either by the photographs shown on figure 15 or by the trace of the flame photographs through a narrow slit in the bomb on a film on a rotating drum. The flame velocity S_s corresponding to the tangent of the angle of inclination of the flame trace to the direction of motion of the film (fig. 16) is determined not only by the propagation of the reaction zone relative to the gas but also by the motion of the gas itself as a result of its propagation in the process of combustion. The degree of this propagation is given by the relation

$$E = \frac{(mr^1)^3}{r}, \text{ where } r \text{ is the radius of the soap bubble at}$$

the instant of inflammation and mr^1 its radius at the end of combustion. The normal velocity of the flame is then $S_t = S_s^1/E$.

The limitation in the application of this method is associated mainly with the effect of the soap film itself (moisture) on the combustion, particularly large for such gases as CO.

Flame propagation in internal combustion engines.— Particularly complicated are the conditions of flame propagation in the internal combustion engine where together with the general reasons for the curvature of the flame front (convection) there are other specific factors, namely, turbulence caused by the passage of the mixture through the suction valve and the motion of the piston in compression and nonuniformity of the temperature of the combustion chamber. Moreover the flame propagation takes place under conditions of changing volume (due to the motion of the piston), changing cross section of the combustion chamber and pressure and temperature of the gas. In short the velocity of flame propagation in the engine depends less on the reaction properties of the mixture and the normal combustion rate than on hydrodynamic factors associated

with the regime of the engine (for example the number of revolutions per minute) and on its design (particularly on the shape of combustion chamber). In connection with this fact the computation of the velocity of flame propagation in the engine for a given normal rate of combustion obtained by any of the described methods should be considered as impracticable.

For the above reason special importance is attached to the methods of direct observation and recording of the flame propagation in the engine with the aid of ionized intervals at various points of the combustion chamber (references 38, 39, and 40) or photographic recording of the flame (references 41 and 42).

In 1936 Rassweiler and Withrow (references 43 and 44) (General Motors Co.) developed an apparatus by which it was possible to obtain up to 2000 flame photographs per second through a quartz window in the engine head (fig. 17). A series of photographs for one cycle for normal engine speed as shown in figure 18 makes possible not only the determination of the velocity of flame propagation but also the changes in the flame front in the process of combustion. One of the effective applications of this method is the possibility of visual observation of the entire process of combustion in the cylinder by the slow projection of such a film on the screen.

Finally, simultaneously with photographing of the flame the recording of the changes in pressure has led to the establishment of an important relation between the volume and the mass of the fuel charge. This makes it possible, for example, to determine directly by the indicator diagram which part of the charge has burned at any stage of the cycle, as shown in figure 19.

RETARDED LUMINOSITY OF THE FLAME AND TEMPERATURE GRADIENT

The attention of investigators has frequently been drawn to the phenomenon of a more or less intensive after-luminosity arising in the products of combustion near the location of the ignition source. By this luminosity instantaneous photographs are taken in the combustion of CO in a spherical vessel with the ignition spark in the center of the vessel (fig. 20)(reference 45). Starting with photograph 5 when the flame front has almost reached the vessel

wall there appears in the center an intensive luminosity gradually spreading to the entire combustible mixture. This does not occur only near the spark but lasts longest there. The authors experimentally investigating the phenomenon of retarded luminosity, are inclined to ascribe it to the burning of the non-reacting parts of the carbon, the heightened intensity being explained by the combustion under relatively higher pressures and temperatures.

A more correct explanation of the phenomenon of retarded luminosity was given by Lewis and Von Elbe (loc. cit. 166-176) associated by them with the formation of a temperature gradient in the products of combustion, as was theoretically shown by Hache (reference 46). The occurrence of a temperature gradient becomes clear from observation of the combustion of the small initial portion of the charge near the ignition spark and the last part of the charge at the wall of the vessel. The fundamental difference in the combustion of these parts of the charge lies in the fact that the combustion of the initial part occurs with propagation at a pressure almost equal to the initial (for example, at $p_i = 1$ atm) and is subject to a compression, during the process of combustion at higher pressures, increasing from p_i to p_{max} (for example, from 1 to 8 atm). The work in compression for this part of the charge is consequently considerably higher than the work in propagation. On the other hand, the last part of the charge is at first subject to compression from p_i to p_{max} and then burns with propagation at p_{max} . In this case the work in propagation is greater than the work of compression. In short the first part of the charge receives a certain excess of energy as compared with the last part of the charge. At complete equality of pressure through all the charge the initial part of the charge is at a higher temperature than the last part.

An idea as to the probable magnitude of the temperature gradient can be obtained from the simplified computation of Ribaud (reference 47) for the combustion of the mixture $\text{CO} + \frac{1}{2} \text{O}_2 + 2 \text{N}_2 = \text{CO}_2 + 2 \text{N}_2 + 68$ calories. With the initial temperature $T_i = 300^\circ \text{K}$ the temperature after combustion of the initial part of the charge (with simultaneous propagation, that is, at $p \sim \text{const}$) is approximately (without taking dissociation into account):

$$T_{\text{initial}} = 300 + \frac{68000}{13.3 + 2 \times 8.1} = 2650^\circ \text{K}$$

The subsequent compression from the initial pressure (1 atm) to the final (8 atm) raises the temperature of the initial part of the charge to

$$T_{\text{initial}} = 2650 \times 8^{\frac{0.4}{1.4}} = 4900^\circ \text{ K}, \text{ taking } \gamma = \\ c_p/c_v = 1.4. \text{ The temperature of the last part of the charge before burning as a result of the previous compression is } T_{\text{final}} = 300 \times 8^{\frac{0.4}{1.4}} = 560^\circ \text{ K and after combustion}$$

$$T_{\text{final}} = 560 + \frac{68000}{13.7 + 2 \times 8.3} = 2800^\circ \text{ K}$$

Thus the temperature gradient between the initial and last parts of the charge is 4900° to $2800^\circ = 2100^\circ$.

Actually (due to dissociation) the difference in these temperatures is considerably less. Thus for the case of the explosion of ozone Lewis and Von Elbe (loc. cit. 175) obtained a temperature gradient 2552° to $1825^\circ = 727^\circ$. In any case it is sufficiently large to explain the increase in the luminosity in the central portion of the charge.

The existence of a temperature gradient has been shown by Withrow and Rassweiler (reference 48) by the direct measurement of the temperature of the gas in an engine provided with windows by the method of sodium line reversal. The light from a heated tungsten filament the temperature of which may be measured and varied within wide limits is admitted through the charge, to which have been added traces of sodium and into the slit of a spectroscope. By means of a stroboscopic disk that instant of the cycle is determined at which the measurement is made. A number of successive photographs of the spectrum with gradual increase in temperature of the light source show, as is seen on figure 21, the temperature at which the reversal of the lines occurs (for which the temperature of the gas becomes equal to the temperature of the light source). In the given case it lies between 3815° and 4015° F (that is, between 2120° and 2230° K).

Finally on figure 22 are shown the temperature data for normal and detonating combustion in the initial and latter parts of the charge. The temperature gradient reaches a particularly large value in detonation (corresponding to the large increase in combustion pressure) so that the temperature of the burning gas at the spark plug

exceeds the flame temperature in the last part of the charge by 390° C. As pointedly expressed by Boyd "the highest temperature appears not in the flame but in the ashes."

The temperature gradient in the gas leads to a more intensive heating of the part of the combustion chamber near the spark plug. According to the measurements of Peletier (reference 49)(at the experimental station at Delft) the temperature of the cylinder head walls is here 50° higher than at the opposite end of the combustion chamber. The heating of the spark plug electrodes caused by the temperature gradient constitutes the danger, particularly great for an airplane engine, of preignition, a phenomenon which leads to a sharp lowering in the engine power and even to the stopping of the engine. To prevent this it is necessary to increase the heat conduction from the spark plug electrodes and the parts near them and also to equalize the temperature gradient by a more intensive turbulence of the charge.

FLAME VIBRATION

The transition from the smooth continuous motion of the flame to vibrational combustion had already been observed by Mallard and Le Chatelier. The flame vibration, as shown by Kirkby and Wheeler (reference 50) is accompanied by fluctuations in pressure of the same frequency not only in closed but in open tubes for which the pressure may be equalized. In this connection the tests of Coward (reference 51) carried out in tubes of various diameters — from 10 to 30 centimeters — and of lengths from 5 to 30 meters are particularly instructive. The photographic recordings shown in figure 23 of the propagation of the flame with the corresponding pressure diagram were obtained for the combustion of a methane-air mixture (10 percent methane) in a 5 meter tube open at the ignition end.

The dependence of the frequency of the vibrations on the length of the tube and the presence of harmonics in addition to the fundamental frequencies show that vibrational combustion is associated with the resonance vibrations of the gas column. The tests of Coward and Hartwell have shown that the possibility of the occurrence of vibrations and the amplitude of the latter, to a strong degree, depend also on the condition of release of the explosion pressure. Thus by gradually moving up a plate to the open

end of the tube the authors obtained a number of pressure recordings shown in figure 24. The diagrams show the place of occurrence of the vibrations and their frequency and amplitude (the right-hand scale). The vertical trace indicates the instant of ending of the combustion - when the flame front of the closed tube reaches the end of the tube (length of tube 5 m, $d = 10$ cm).

The first diagram was obtained under conditions corresponding to figure 23, that is, at full opening at the ignition end of the tube. The vibrations die down and finally completely vanish on placing in front of the open end of the tube a plate with a small aperture (about 15 mm) or a piece of glass wool. At full closure of the tube, however, vibrations again arise with a considerable increase in the amplitude and rise in the rate of combustion. The same change in the conditions at the ignition end - a gradual decrease in the aperture - in a tube of diameter 30 centimeters did not lead to a suppression of the vibrations but only to an earlier occurrence.

The practical significance of these tests is directly connected with the explosive effect of vibrations, and on the basis of their results obtained in tubes of small diameter (about 10 cm) the authors recommend protective screens with a certain aperture by which the vibration can be suppressed.

Many investigators have attempted to associate vibrational combustion with "knocking" in the engine.* This, however, has been disproved by direct investigation of detonating combustion in the engine and also by the further study of vibrational combustion itself.

By comparing the amplitude of the pressure fluctuations arising in combustion in a bomb for various fuels Küchling (reference 52) came to the conclusion that "the chemical structure of the fuels and also their associated physical properties, for example, the self-ignition temperature (and we may add the detonation characteristics) contrary to all expectation show only an entirely negligible effect on the occurrence of vibrations (or as the author calls them the phenomenon of knock) in the bomb."

It is sufficient to show that the amplitude of vibration for benzol, toluol, or ethyl alcohol (a fuel with maximum detonating stability) was the same as that for heptane.

*For a discussion of these papers see article by Sokolik and Voynov (reference 42).

It was moreover observed by Küchling that the partial substitution of nitrogen by oxygen leads to a suppression of vibration with a simultaneous increase in the rate of combustion. The necessity for the occurrence of vibration at some quite definite speed of combustion corresponding to conditions of resonance is indicated by the fact that with hydrogen the maximum amplitudes of vibration were observed both with the mixture with maximum speed of combustion (36 percent H₂, speed of the flame 35 m/sec) and with the limit of inflammability (10 percent H₂, speed of the flame about 1 m/sec).

Lewis and Von Elbe (loc. cit. 317) reject any connection of vibrational combustion with the phenomenon of resonance and assert, for example, that (under certain conditions) "the phenomenon of vibrations does not depend on the size and shape of the vessel." This statement is simply untrue. Their own very few experiments with hydrogen-air mixtures led them to the conclusion that the occurrence of vibrations was associated with the presence of excess oxygen or nitrogen, particularly of the first (we may note that vibrations with maximum amplitude were observed by Küchling also in mixtures with oxygen deficiency). An original explanation of vibrational combustion is proposed by Lewis and Von Elbe, namely, that it is due to an "excitation lag," a lag in the establishment of uniform distribution of energy between the kinetic and internal (vibrational) energies of the molecules O₂ and N₂. This lag and consequently the abnormal excesses of kinetic energy is greater the lower the combustion temperature and for this reason according to the authors it should be particularly sharp in strong dilutions with oxygen and nitrogen. The "excitation lag" denotes a certain change in the heat capacity with time, namely, its gradual increase with establishment of equality of energy distribution. The transformation of an excess of kinetic energy into vibrational should be related to the lowering of the pressure in accordance with the equation:

$$\frac{3}{2} p v = N \frac{1}{2} \overline{m v^2}$$

The heating of the internal gas layers due to compression in the process of combustion leads to a rapid establishment of uniform energy distribution and to a decrease in the volume of this part of the burning gas; hence the formation of a mass gas flow directed inwards and the occurrence of pressure waves.

In evaluating the above hypothesis account should be taken of the fact that it proceeds from the necessary existence of those conditions which produce a temperature gradient in the products of combustion and which arise naturally only in closed vessels. Vibrational explosions, however, as follows from the tests of Coward and many other investigators as far back as Mallard and Le Chatelier, are also observed in open tubes where these conditions do not obtain, where there is no adiabatic compression of the gas increasing with the combustion and a corresponding increase in the temperature of the nucleus and where, on the contrary, the temperature of the combustion products is continually lowered due to heat transfer. For this reason the hypothesis of Lewis and Von Elbe at the most may have limited application to the case of combustion of lean mixtures in closed tubes.

DETONATION

Structure of explosion wave.— According to the classical concepts (reference 53) as to the causes underlying detonation or explosion waves the latter represents a simultaneous propagation with the same velocity (exceeding the velocity of sound) of a shock wave (that is, a wave with an instantaneous large increase in pressure) and a combustion wave. An exact coinciding of both wave fronts was generally assumed, as schematically represented in figure 25A. This means that the instantaneous pressure produced by the shock wave should give rise to an instantaneous (that is, with zero lag) self-ignition of the gas mixture.

The propagation of a combustion wave with the same velocity as the shock wave leads to the following fundamental differences between detonating and normal combustion:

1. In detonating combustion self-ignition of the gas arises from adiabatic compression of the gas by the shock wave according to the dynamic adiabatic of Hugoniot which differs from the usual Poisson adiabatic as shown in figure 26 by the higher increase in the pressure for the same decrease in volume.
2. In detonating combustion the condition of mixture ahead of the explosion wave front remains

unchanged and the self-ignition conditions of each layer of the gas also remain unchanged. The explosion wave thus represents in its very nature a stationary type of combustion propagation.

3. Finally in detonating explosion a continuous equalization of the pressure throughout the volume of the gas occurring simultaneously with the flame propagation is not possible (as with normal combustion) since the pressure wave is propagated simultaneously with the flame front and with the same velocity.

The investigations of recent years have led to a fundamental correction in the concepts as to the structure of the explosion wave. Different authors almost simultaneously and independently of one another came to the same conclusion, namely, that in the detonation wave there always, except perhaps for special cases, occurs a certain interval between the explosion wave front and that of the combustion wave as schematically represented in figure 25B.

Bone and his coworkers (reference 54) in 1935 published the results of an extensive investigation on the structure of a detonation wave which he studied with the aid of a new high-speed photographic Fraser camera, figure 27. The flame is photographed on a stationary film with the aid of a mirror silvered on both sides and rotating in an evacuated chamber (to decrease the resistance at the high rotative speed of the mirror). The apparatus gives a record corresponding to a linear velocity of the picture on the film up to 1000 meters per second. The photograph shown in figure 28 gives a detailed analysis of the process of formation of explosion waves in the mixture $2CO + O_2$ notwithstanding the fact that the entire process lasts no longer than 10^{-4} second.

The self-ignition in a shock wave initiating the detonation occurs at the distance of 64 millimeters from the flame front. From the point of view of Bone this distance is the maximum within which "the radiation from the flame front, absorbed by the compressed gas in the shock wave, may lead to such rise in the temperature and intensity of activation of the molecules as will result in self-ignition in the shock wave" (loc. cit. 39).

Although an interval between the flame front and the place where the detonation wave arises was observed by Bone with sufficient distinctness only for carbon monoxide the observation provided him with a basis for reaching a general conclusion that "the detonation wave must be looked upon as the more or less stable combination of two separate and separable components, namely, an intensively luminous flame front and an invisible shock wave immediately ahead of it" (loc. cit. 31).

The instability of the explosion wave and the "separateness" of both components of the same mixture is proven by Bone by a number of phenomena. Thus on decreasing the diameter of a tube to 3.6 millimeters (near the limiting diameter for the propagation of the explosion wave) there is observed a periodic extinction of the detonation wave "as a result of the cooling effect of the walls." The same periodic extinction of the detonation wave occurs on passage of the waves through a narrow layer of nitrogen (about 6 mm) the velocity of the wave dropping from 1800 to 700 miles per second, or on placing a section of the explosion tube in the field of a powerful electromagnet directed along the tube axis (a drop in the velocity by 90 m/sec) or finally on passage through an electric field (the velocity drops to almost half its value particularly in the passage of the wave from the cathode to the anode explained by Bone as due to the drawing off from the wave front of C + O ions). All these tests according to Bone show that even a slight slowing in the flame front (due to the action of one of the factors given above) leads to a complete breakdown of the unstable relation between the combustion zone and the wave front and to a complete separation of the forward shock wave from the flame front. In his conclusions Bone does not remark on any possible relation between the structure of the explosion wave and the kinetic properties of the mixture although his tests do give some indication of such a relation. We may note that neither the characteristic "interval" during the occurrence of the detonation wave (self-ignition ahead of the flame front) nor the extinction of the wave in passing through an electric field were obtained for many other oxygen mixtures investigated by Bone, such as hydrogen and methane.

The relation between the structure of the detonation wave and the kinetic properties of the mixture is most clearly brought out by the detonation limits, that is, by mixtures of the limiting concentrations at which detonation waves may arise. A systematic investigation of the

detonation limits in our laboratories (references 55 and 56) has provided frequent examples of the fact that the unstable character of the detonation wave is closely connected with the chemical characteristics of the mixture; thus, for example, in mixtures of CO with oxygen the limiting detonation wave presents the character of a stable wave when small amounts of hydrogen are added (which fact is associated with the sharply accelerating action of hydrogen on the oxidation of carbon monoxide); on the contrary in mixtures of methane with oxygen the detonation wave becomes less and less stable as the mixture is diluted with nitrogen.

In correspondence with the scheme of figure 25B a stable propagation of a detonating wave is possible under conditions where the self-ignition lag at the pressure and temperature of compression in the shock wave does not exceed a certain limiting value, otherwise the gas layer is in a rarefaction zone following the compression (in the shock wave) and cools before self-ignition can occur. Thus notwithstanding the extremely small time interval during which the gas is traversed by the shock wave the possibility of its self-ignition (and this is the fundamental condition for the existence of an explosion wave) will be determined by the kinetics of the oxidizing reactions during compression in the explosion wave. From this point of view some interval between the shock wave front and the combustion wave should occur in every explosion wave and should show up most sharply near the detonation limits.

The greatest direct confirmation of the above conclusions is provided by tests in which through certain small additions of H_2 or C_2H_2 (up to 0.3 percent) to nondetonating mixtures of CO with air a stable propagation of an explosion wave was obtained. The energy of combustion of the mixture remained unchanged but its reaction ability was increased.

The kinetics in the reaction zone can be affected also by varying, for example, the power of the shock wave, that is, by an increase in its pressure and temperature. This is the object of the tests of Payman (reference 57) who first obtained the propagation of an explosion wave in a methane-air mixture by inflammation from a shock wave due to the explosion of a powerful charge of fulminating mercury (50 g). In this connection it would be interesting to obtain a detonation wave in the same methane-air

mixture by the addition of small quantities of NO_2 , the catalyzing action of which on the oxidation and self-ignition of methane is widely known (references 58 and 59).

Detonation spin.— With the structure of the detonation wave there is associated, though not yet clearly, the phenomenon of "detonation spin" giving a characteristic "stratified" structure on the photographs of explosion waves (fig. 29). As far back as 1926 Campbell and his co-workers (reference 60) on the basis of their tests came to the conclusion that such a character of the photographic recordings was due to the motion of the detonation wave front along a spiral path. This among other things is confirmed by the fact that the detonation wave leaves a spiral trace on the walls of a tube covered by a layer of silver or lead, the pitch of the spiral exactly agreeing with the pitch measured on the photographs.*

The assumption was natural that the "spin" was connected not only with the spiral motion of the combustion zone but also with the motion of the gas. The method of high-speed photographic analysis with the aid of the Fraser apparatus showed, however, the incorrectness of this assumption and has led to a new treatment of the phenomenon of detonation spin. The photograph in figure 30 of a detonation wave in a mixture of $2\text{CO} + \text{O}_2$ shows that the "stratified" structure which we see on figure 29 actually presents, as the authors write, a "secondary effect" formed by the intersection of two series of lines, one of them due to luminous particles moving ahead of the wave front with a velocity of 780 meters per second (this is the mass velocity u forming one of the velocity components of the detonation wave: $D = u + c$, where c is the velocity of sound at the corresponding temperature); the second series of lines is the trace of the compression waves traveling through the heated medium with the resultant velocity 320 meters per second (this velocity is equal to 1100 to 780 m/sec, that is, the difference between the true velocity of the compression wave and the oppositely directed velocity of the gas). This shows that during each complete rotation of the detonation wave there is a sudden inflammation of a portion of the gas at the instant when the shock wave front passes through or immediately thereafter (loc. cit. 38).

*For a review of these papers see my monograph, "Combustion and Detonation in Gases." pp. 43-49, 1934.

On the basis of these detonation tests the detonation wave must be considered not as continuous process of combustion wave propagation simultaneously with the shock wave but as a periodic self-ignition of the gas caused by the shock wave.

The observations of various investigators indicate a direct relation between the periodic character of detonating combustion and a wave structure such that it is possible to assume a more or less considerable interval between the self-ignition point and the shock wave front. Thus in the tests of Bone and Fraser (reference 61) the "spin" is always observed near the occurrence of the detonation wave; whereas in the steady wave it is absent in some mixtures (or in any case not observed). The extinction of the detonation wave in passing through a layer of an inert gas or an electric or magnetic field also refers only to a wave with a "spiral" structure.

In the tests of Bréton (reference 62) and our own (reference 55) spin was almost always observed in mixtures near the detonation limits (including hydrogen mixtures), that is, where self-ignition in the detonation wave occurs with maximum possible lag and vanishes as this lag is reduced by adding, for example, hydrogen to mixtures of carbon monoxide.

Attempts at a theoretical analysis of the phenomenon of detonation spin (references 63 and 64) so far have only a qualitative character and lead practically to the establishing of a periodic self-ignition in the shock wave with a certain lag but in no way explain the occurrence of rotation of the detonation wave front.

We may note, finally, that the propagation of detonation waves in solid explosive substances likewise gives a spiral trace (reference 65) explained by Muraour (reference 66) as due to the occurrence in the gas at supersonic speeds of periodic alternations of compression and rarefaction.

Detonation in the internal combustion engine.— The application in our laboratories of the high-speed photographic method to the investigation of combustion in the engine has led to the establishment of a fundamentally important fact, namely, the formation in the engine under knocking conditions of an explosion wave with all its characteristic properties (reference 42). With this was concluded a certain stage in the investigation over many years

of the nature of detonation in the engine and again the question was raised as to the mechanism of its occurrence. At the same time our tests led to a number of new attempts at treatment of the detonating combustion in the engine such that it would not be necessary to identify such combustion with an explosion wave. In describing detonation waves large use is made of the tests of Withrow and Rassweiler with their high-speed camera recordings.

Figure 31 shows six series of photographs obtained on a detonating test engine (see fig. 17) starting from the instant directly preceding the detonating explosion. Up to this instant the flame propagation in no way differs from the normal regime of the engine. The authors note as a characteristic property of detonating combustion the appearance of a flame center (or centers) ahead of the primary flame front indicating self-ignition in the last part of the charge. On this basis it is stated that "knock is certainly not the result of a sudden increase in the velocity of propagation ahead of the flame" but is the almost instantaneous propagation of the flame from the self-ignition center. Finally, it is remarked that the "detonating self-ignition" of the last part of the charge leads to a sharply accelerated motion of the gas in the main part of the combustion chamber and directed toward the spark plug.

Just what is new in these observations? They show first of all that the flame under knock conditions envelopes the last part of the charge for a time less than the interval between two successive exposures (2° rotation of the crankshaft, corresponding at 900 rpm to $1/2700$ sec). This can give only a lower limit of the velocity of flame propagation in knock, namely, that it is above 180 meters per second. At the same time our measurements conducted at considerably higher recording velocity (accurate to 0.1° of shaft rotation) give the true magnitude of this velocity as 2000 meters per second.

As regards the place of origin of the detonation our recordings (fig. 32) likewise show with great clearness that self-ignition often accompanies detonation waves propagated at a small velocity. The detonation wave may arise simultaneously both from the primary flame front and from the secondary formed during self-ignition. (See fig. 32C.) Finally of special importance is our observation that at relatively early self-ignition the occurrence of detonation generally becomes impossible.

In 1938 Laffitte (reference 67) proposed a new description of detonating combustion in the engine (to explain the wave velocities obtained by us) on the basis of his analogy with the phenomenon of "flame rejection." By exploding a detonating mixture of butane or acetylene with oxygen in a glass tube separated from another open tube by a thin celophane diaphragm Laffitte obtained photographs similar to those shown in figure 33.

Fundamentally these are the usual photographs of detonation waves arising as a result of a predetonation travel of the flame (see below) and sharply differ from the photographs of detonating combustion in the engine where the sudden formation of detonation waves is characteristic. Laffitte, however, calls attention to the fact that here self-ignition arises at the place of the celophane rupture (which fact as we have seen indicates a special structure of the explosion wave) and that the propagation of the flame with the detonation velocity (1700 to 1900 m/sec) takes place in the second, open tube (in a small part of it) in the gas immediately after the diaphragm rupture. An analogous flame ejection with increased velocity occurs according to Laffitte also in the engine from the self-ignition centers forming the so-called "dissociating detonation" (a term of Jouget identical with the concept of a finite interval between the shock wave and combustion wave fronts (reference 67a).

The "theory" of Laffitte widely acclaimed in France* in no way offers anything new as to the nature of detonating explosion in the engine as announced by the author but only repeats the conclusions of Withrow and Rassweiler regarding the position of origin of detonation, making use of an entirely arbitrary analogy between combustion in the engine and in tubes.

Finally Broeze (reference 68) (director of the experimental station at Delft) proposes still another explanation of our tests as schematically presented in figure 34a. This author writes: "When the secondary flame (from self-ignition at centers 4 to 5) is propagated from the lateral part of the chamber its front may cut out a narrow field of view in the window under a certain angle so that the measurement of the velocity as presented by Sokolik and Voynov is incorrect."

*See the article in *Nouvelles de la chimie*, March 1939, no. 51.

This curious interpretation of our photograph records is partly due to an insufficient study of them for otherwise the author would observe also the occurrence of a "retonation" wave (see fig. 34b) which cannot be explained as an optical illusion, and partly to a strange assumption that in all the tests the secondary flame front by chance passes through the field of view always under the same angle corresponding to the detonation velocity. Finally the explanation of Broeze is conveniently silent regarding the source of formation of reflected shock waves which, as we have shown, are formed by the detonating and retreating waves and a long time after the end of combustion are still propagated in the cylinder with supersonic velocities.

Thus our test results indicating the formation in the knocking engine of an explosion wave are in no way shaken by the succeeding investigations and as before must lie at the basis of modern concepts as to the nature of detonation in the engine.

How then is the mechanism of detonation in the engine to be pictured? It is necessary first of all to note particularly the principal differences in the processes of formation of detonation waves in oxygen mixtures in the tube and in the engine. In the first case a shock wave arises through the accumulation of successive compression waves. This process, theoretically described by Jouget (reference 53) and Becker (reference 69), was experimentally reproduced by Payman (reference 70) with the aid of the Toepler method permitting the observation of compression in the gas after the passage of a compression wave (making use of the change in optical density of the medium).

The photograph recordings in figure 35 show that the detonation wave in tubes arises at the place where a series of compression waves unite and as a result of the flame dispersal in the predetonation period. That another source must be assumed for the formation of a shock wave in the engine follows from the fact that the propagation of the flame before the occurrence of the detonation in this case in no way differs from the combustion under normal engine conditions and, as shown by our photograph records, and those of Withrow and Rassweiler, the propagation takes place at a small velocity (15 to 20 m/sec). This and a number of other considerations* forces us to the conclusion that the

*See my article in Progress in Chemistry (USSR), 7, 976, 1938.

formation of the explosion wave in the engine is entirely conditioned by a preinflammation oxidizing process in the last part of the charge.

Without going into the chemistry of this process, we may remark merely that it is analogous to the preinflammation processes which take place in the first stage of the induction period in the self-ignition of hydrocarbons in the low-temperature zone (see fig. 7) and which consist essentially in the accumulation of critical concentrations of the active products of the intermediate oxidations (peroxides). It must be assumed that these products are not uniformly distributed over the entire volume of the last part of the charge but, as always occurs in preignition oxidations, are localized in individual portions of it. The inflammation of these centers with critical concentrations of peroxides by the flame front tongues should occur with a limiting short lag and with the formation of a local sharp pressure rise. This is the shock wave initiating the explosion wave in the remaining part of the charge.

This mechanism of the formation of the shock and detonation waves in the engine differs from the "nuclear" theory of detonation recently proposed by Serruys (reference 71) in this essential respect, namely, that the latter theory considers the formation of the shock wave as an immediate result of the inflammation of individual centers (nuclei) due to their heating, an assumption which, as we have seen, contradicts direct observations.

The proposed explanation leads to the interesting conclusion that one of the effective methods of suppressing detonation in the engine may be an intensive mixing of the last part of the charge thus preventing the formation of local centers with high concentration of peroxides. This is possibly the explanation of the notable antidetonating properties of the combustion chamber construction of Serruys shown in figure 36. The concentric grooves, from this point of view, not so much increase the cooling of the last part of the charge (to which Serruys himself ascribes the antidetonating effect) as make possible a turbulence and mixing of the charge thus rendering difficult the formation in the chamber of "detonating inflammation."

REFERENCES

1. Semenoff, N. N.: Chain Reactions. Goschimtechizdat, L., 1934.
2. Norrish, R. G. W.: Proc. Roy. Soc., 150, 36, 1935; 157, 503, 1936.
3. Sachsse: Chemical Progress. (USSR) 7, 436, 1938.
4. Van't Hoff, J. H.: Outlines of Chemical Dynamics. 1936.
5. Dixon and Bradshaw: Jour. Chem. Soc., 105, 2027, 1914.
6. Norrish, R. G. W.: Proc. Roy. Soc., 135, 334, 1932; Sow. Phys., 3, 225, 1933; Proc. Roy. Soc., 167, 292, 1938.
7. Todes, O. M.: Journal of Physical Chemistry. (USSR) 13, 868, 1939.
8. Frank-Kamenetsky, D. A.: DAN, 18, 411, 1938.
9. Zeldovich and Yalovlev: DAN, 19, 699, 1938.
10. Zagulin, A. V.: Journal of Physical Chemistry. (USSR) 4, 92, 1933.
11. Naylor and Wheeler: Jour. Chem. Soc., 1426, 1935.
12. Townend, D. T. A.: Ignition Regions of Hydrocarbons. Chemical Reviews, 21, Oct. 1937, pp. 259-278.
13. Kravets, Yantovsky, and Sokolik: Journal of Physical Chemistry. (USSR) 13, 1742, 1939.
14. Tizard, H. T. and Pye, D. R.: Experiments on the Ignition of Gases by Sudden Compression. Phil. Mag., 44, (6) July 1922, p. 79.
15. Neiman and Yegorov: Journal of Physical Chemistry. (USSR) 3, 61, 1922.
16. Stern, Kravets, and Sokolik: Journal of Physical Chemistry. (USSR) 11, 706; 12, 69, 1938.

17. Kaulin, Neiman, and Serbikov: Jour. Tech. Phys., (USSR) 6, 1936, p. 183.
18. Kaulin, Michailov, and Neiman: Ignition Tests of Diesel Fuels in a Bomb (Cetene Numbers). Dieselstroyenie, no. 6, June 1936, pp. 4-9.
19. Morozov and Smirnov: Dieselstroyenie, no. 10, 1938, p. 3.
20. Sokolik, A. S.: Acta Physicochimica. (URSS) 11, 1939, 381.
21. Neiman, M. B.: Chem. Prog. (USSR) 7, 1938, 341.
22. Kane, G. P.: The Two-Stage Auto-Ignition of Hydrocarbons and "Knock." Proc. Royal Soc., 167, July 7, 1938, pp. 62-80.
23. Sachsse: Z. Physik. Chem., B-33, 1936, 229.
24. Silver, R. S.: The Ignition of Gaseous Mixtures by Hot Particles. Phil. Mag., (7), 23, Suppl. April 1937, pp. 633-657.
25. Paterson, S.: The Ignition of Inflammable Gases by Hot Moving Particles. Phil. Mag., (7) 28, July 1939, pp. I 1-23.
26. Coward and Hartwell: Jour. Chem. Soc., 2676, 1932; 546, 1933.
27. Coward, H. F. and Payman, W.: Problems in Flame Propagation. Chem. Rev., 21, no. 3, Dec. 1937, pp. 359-366.
28. Mallard et Le Chatelier: Ann. d. Mines, 8, 274, 1883.
29. Voronkov and Sokolik: Journal of Physical Chemistry. (USSR) 6, 1385, 1935.
30. Ribaud et Gaudry: XVIII Congr. de Chim. Ind., Nancy, 1, 18-C, 1938.
31. Chitrin, L.: Tech. Physics URSS, 4, 110, 121, 1937.
32. Gouy: Ann. d. Chim. et Phys., 18, 1, 1879.

33. Michelson, V. A.: Collected Works. Moscow, 1930.
34. Smith, F. A.: Chem. Rev., 21, 389, 1937.
35. Lewis and Von Elbe: Combustion, Flames and Explosions of Gases. Cambridge, 1938.
36. Stevens, F. W.: The Gaseous Explosive Reaction at Constant Pressure. The Effect of Inert Gases. Jour. Amer. Chem. Soc., vol. 50, Dec. 1928, pp. 3244-3258. Jour. Amer. Chem. Soc., vol. 48, 1926, p. 1896. The Gaseous Explosive Reaction - The Effect of Pressure on the Rate of Propagation of the Reaction Zone and Upon the Rate of Molecular Transformation. Report No. 372, NACA, 1930.
37. Fiock, E. F., and Marvin, C. F., Jr.: The Measurement of Flame Speeds. Chem. Rev., 21, Dec. 1937, pp. 367-387.
38. Schinauffer, K.: Z.V.D.I., 75, 455, 1931; SAE Jour., 34, 17, 1934.
39. Abugov and Sokolik: J.E.T.Ph., 3, 438, 1933.
40. Rabezzana and Kalmar: Auto. Eng., 29, 347, 1934.
41. Withrow, L., and Boyd, T. A.: Photographic Flame Studies in the Gasoline Engine. Industrial and Engineering Chemistry, vol. 23, no. 5, May 1931, pp. 539-547.
42. Sokolik and Voynov: Izvestia AN SSSR, OMEN, 123, 1937.
43. Rassweiler, G. M., and Withrow, L.: Slow Motion Shows Knocking and Non-Knocking Explosions. SAE Jour., vol. 39, 1936, pp. 297-303, 312.
44. Rassweiler, G. M., and Withrow, L.: High Speed Motion Pictures of Engine Flames Correlated with Pressure Cards. SAE Jour., vol. 42, May 1938, pp. 185-204.
45. Ellis and Wheeler: Jour. Chem. Soc., 310, 1927.
46. Mache: Die Physik der Verbrennungerscheinungen, Leipzig, 1918.
47. Ribaud: Chaleur et Industrie, 20, 15, 1939.

48. Rassweiler, G. M., and Withrow, L.: Flame Temperatures Vary with Knock and Combustion-Chamber Position. SAE Journal, vol. 36, Apr. 1935, pp. 125-136, 146.
49. Peletier: Chaleur et Industrie. Discussion. 20, 1939.
50. Kirkby and Wheeler: Jour. Chem. Soc., 847, 1931.
51. Coward, Hartwell, and Georgeson: Jour. Chem. Soc. 1482, 1937.
52. Küchling, A.: Z.V.D.I., 82, 1126, 1938.
53. Jouguet, E.: Mécanique des Explosifs. Paris, 1917.
54. Bone, W. A., Fraser, R. P., and Wheeler, W. H.: A Photographic Investigation of Flame Movements in Gaseous Explosions. Part VII-The Phenomenon of Spin in Detonation. Phil. Trans., Roy. Soc. of London. Vol. 235, 1935, pp. 29-68.
55. Riven and Sokolik: Journal of Physical Chemistry. (USSR) 7, 571; 8, 767, 1936; 10, 688, 692, 1938.
56. Sokolik, A.: Jour. Phys. Chem. (USSR), 13, 1031, 1939.
57. Payman, W., and Shepherd: Proc. Roy. Soc., 153, 348, 1937.
58. Norrish and Wallace: Proc. Roy. Soc., 145, 307, 1934.
59. Coward, H. F.: Jour. Chem. Soc., 1382, 1934.
60. Campbell, Finch, and Woodhead: Jour. Chem. Soc., 1925, 3010; 1572, 1927; 2094, 1928.
61. Bone, W. A., Fraser, R. P.: Phil. Trans., 230, 363, 1931.
62. Bréton, J.: Thèses, Nancy, 1936.
63. Becker, R.: Z. Elektrochem., 42, 457, 1936.
64. Jost, W.: Z. Physik. Chem., B 42, 136, 1939.

65. Urbanski: Z. Ges. Schiess.-u. Sprengst., 22, 270, 1927.
66. Muraour: Chimie et Industrie. 42, 604, 1939.
67. Laffitte, P.: La Propagation des Flammes dan les Mélanges Gazeux. Paris, 1939; C.R., 206, 603, 1648, 1938.
- 67a. Jouguet, E.: La Science Aérienne. 3, 138, 1934.
68. Broeze, Van Driel, and Peletiez: Schriften der Deutsch. Akademie der Luftfahrtforschung. Heft 9, 1939.
69. Becker, R.: Impact Waves and Detonation. T.M. Nos. 505 and 506, NACA, 1929.
70. Payman, W. and Titman, H.: Explosion Waves and Shock Waves. Pt. III: The Initiation of Detonation in Mixtures of Ethylene and Oxygen and of Carbon Monoxide and Oxygen. Proc. Roy. Soc., 152, Nov. 1, 1935, pp. 418-445.
71. Serruys, M.: La Combustion Détonante dans les Moteurs a Explosions. Paris, 1937.



Figure 1.- Self-ignition in an adiabatic bomb (Dickson and Bradshaw).

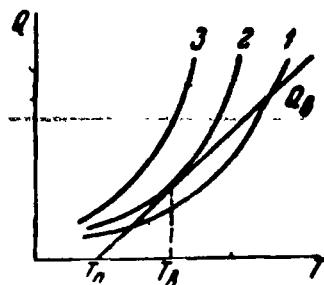


Figure 2.- Derivation of the limiting conditions of self-ignition (Semenoff).

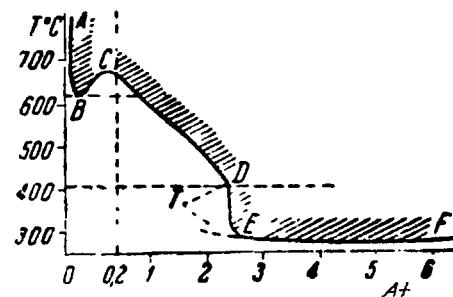


Figure 3.- Limits of the region of self-ignition of hydrocarbons within a large pressure interval. The dotted lines (T) denote the limits according to Townend.

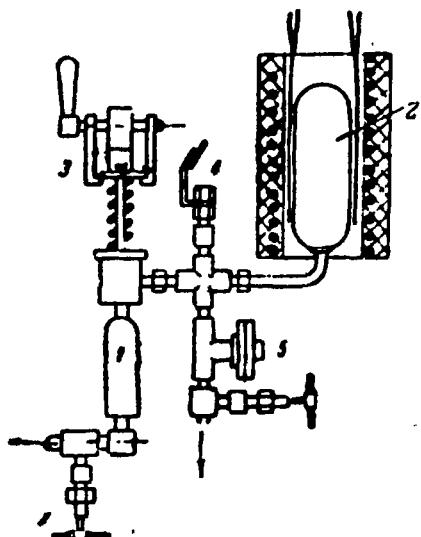


Figure 4.- Sketch of apparatus for the investigation of self-ignition.
 1, prechamber;
 2, bomb;
 3, quick-action valve;
 4, window for visual observation;
 5, diaphragm manometer.

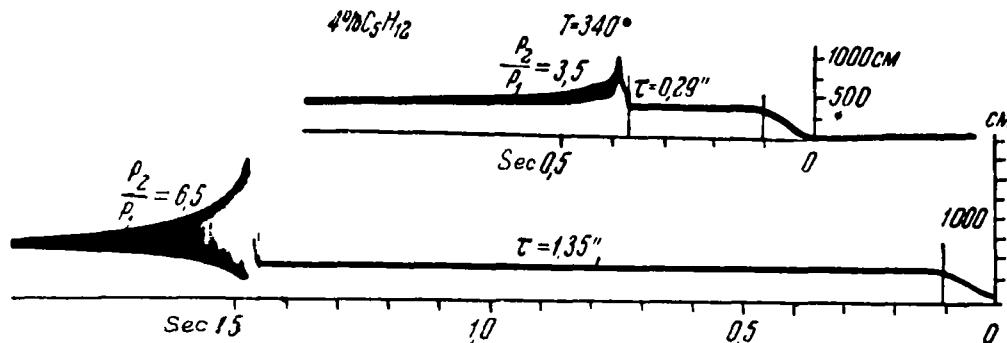


Figure 5.- Examples of pressure recordings during self-ignition.

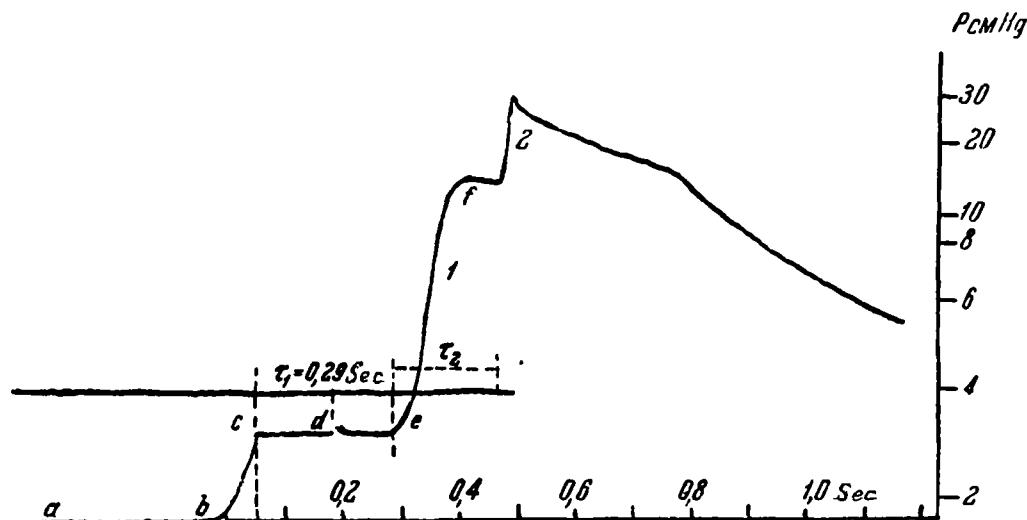


Figure 7.- Pressure diagram obtained with the aid of the differential indicator for the self-ignition of heptane (tests of Kravets and Yantovsky). 1, cold flame; 2, hot flame.

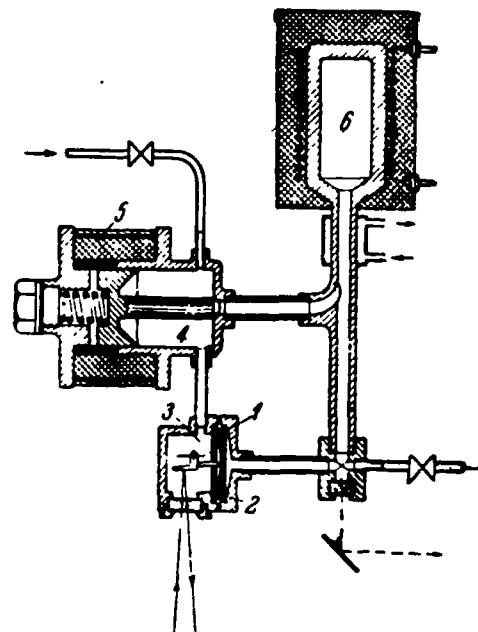


Figure 6.- Differential optical manometer for the study of the kinetics of the explosion process (design of A. N. Voynov and A. I. Bikov).

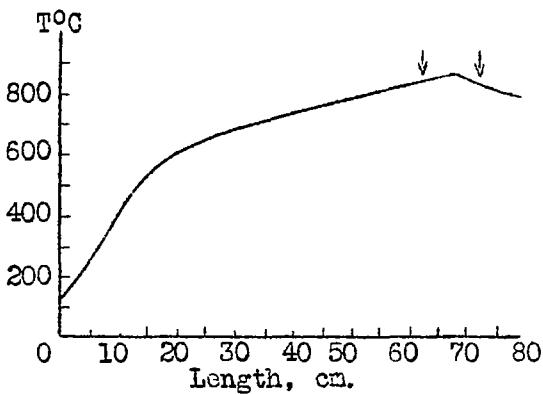


Figure 8.- Temperature distribution in a tube according to tests of Sachsse.

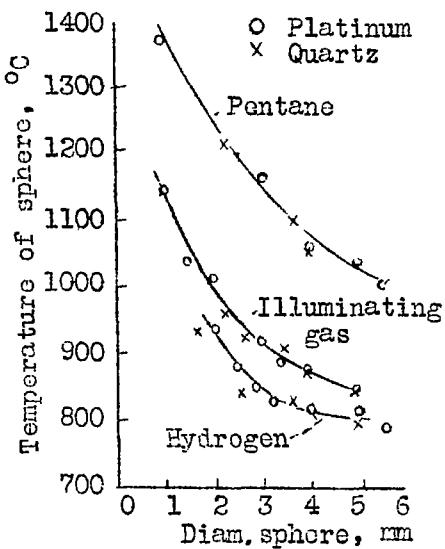


Figure 10.- Effect of the diameter of the particles on the self-ignition temperature of gases for $\tau \sim 0$ (Silver).

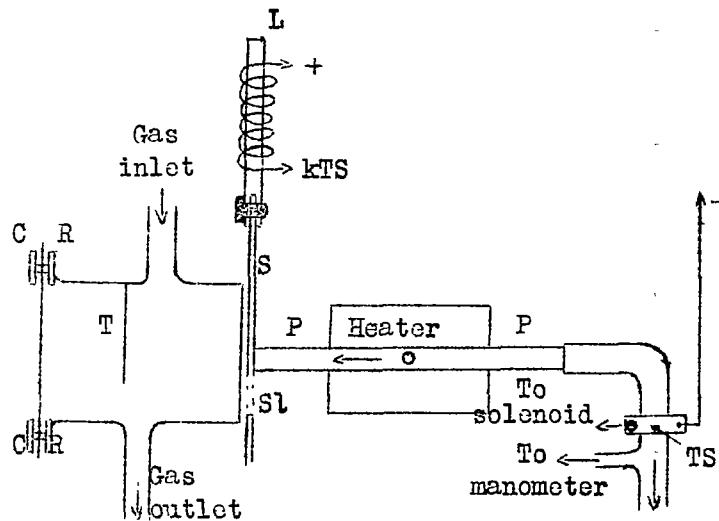


Figure 9.- Set-up for the investigation of self-ignition of a gas by heated particles.

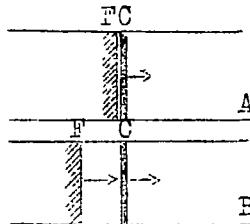


Figure 25.- Schematized explosion wave: A- exact coincidence of the flame front (F) with the front of the shock wave (C); B- with an interval between them.

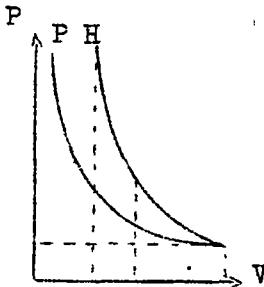


Figure 26.- Hugoniot adiabatic (H) and Poisson adiabatic (P).



Figure 11.- Explosion of coal dust in a mine opening. Top- ejection of dust cloud; bottom- flame front.

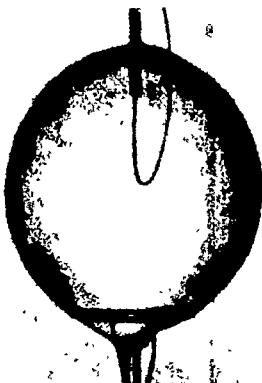


Figure 14.- Soap bubble in which flame propagation at constant pressure is observed.



Figure 12.- Series of instantaneous photographs of flame propagation in tubes (Coward and Hartwell).



Figure 13.- Increase in cone area of the flame on lowering the normal combustion velocity (Chitrin).

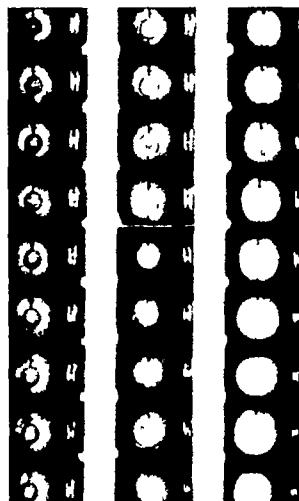


Figure 15.- Instantaneous photographs of a spherical flame front for combustion in a soap bubble (Flock and Marvin).

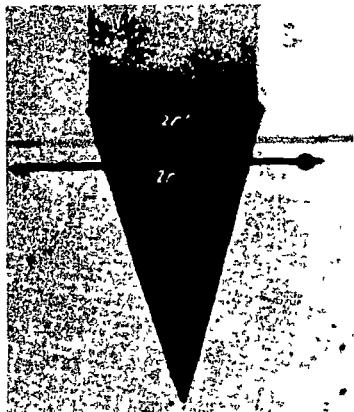


Figure 16.- Flame propagation in a soap bubble developed on a moving film (Stevens).

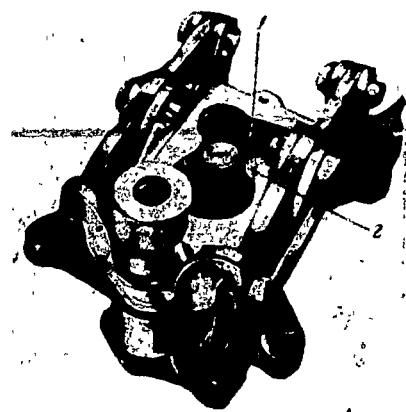


Figure 17.- Head of a single-cylinder engine with quartz top (Withrow and Rassweiler) 1. spark plug 2. intake valve

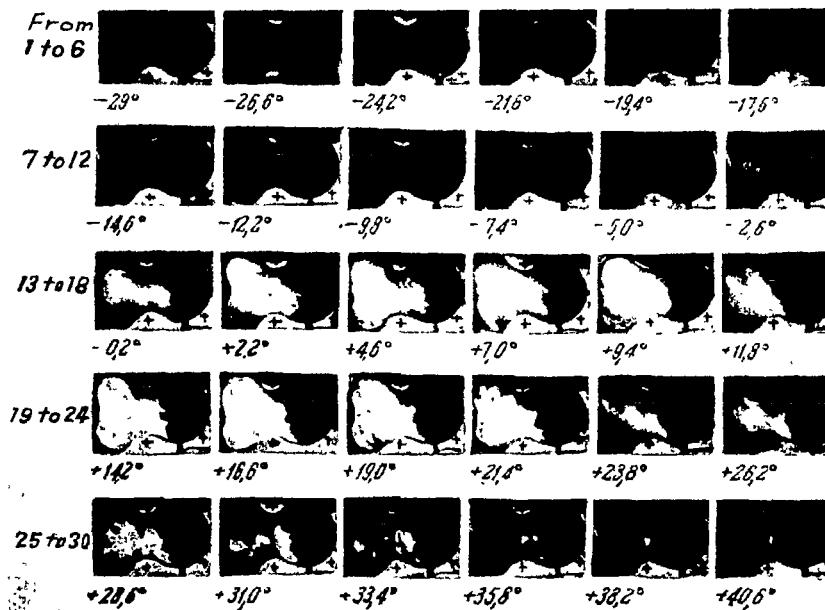


Figure 18.- Series of instantaneous photographs of the flame front for normal operation of the engine (Withrow and Rassweiler).

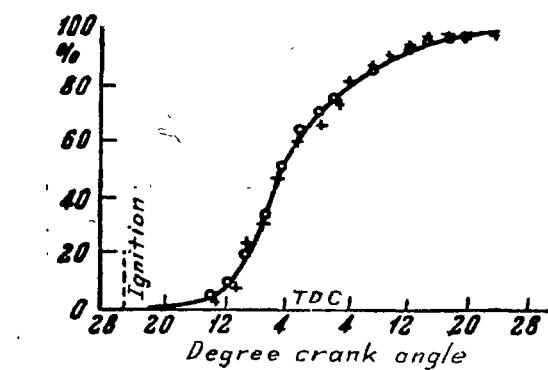


Figure 19.- Relation between the increase in pressure due to combustion (%) and the mass of burning charge (+); TDC- top dead center (Withrow and Rassweiler).

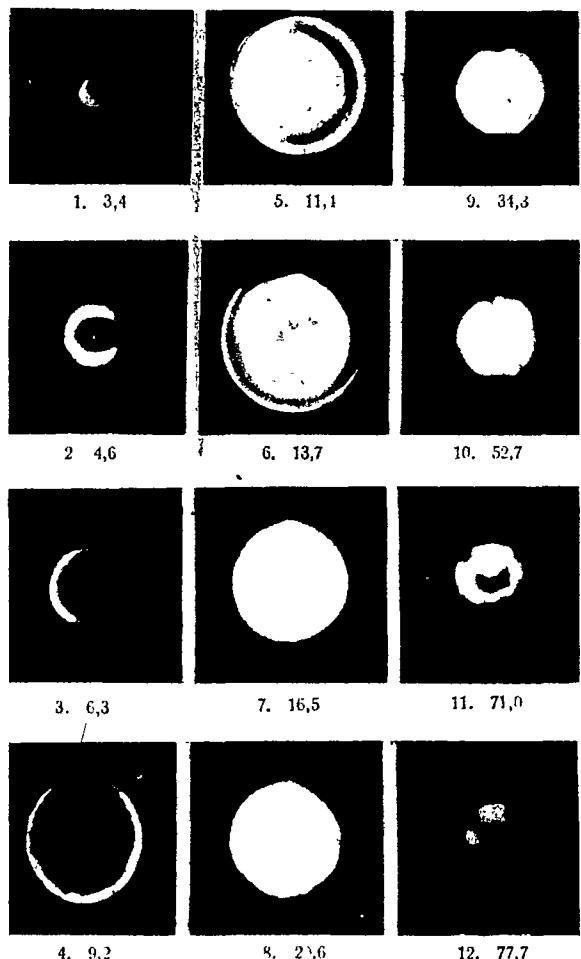


Figure 20.- Series of instantaneous photographs with retarded luminosity for the combustion of carbon monoxide (Ellis and Wheeler). The figures under each picture denote the time from the instant of flash in thousandths of a second.

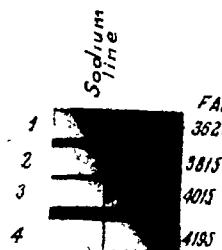


Figure 21.- Spectrum showing the reversal of the sodium lines on gradually increasing the temperature of the light source (Withrow and Rassweiler).

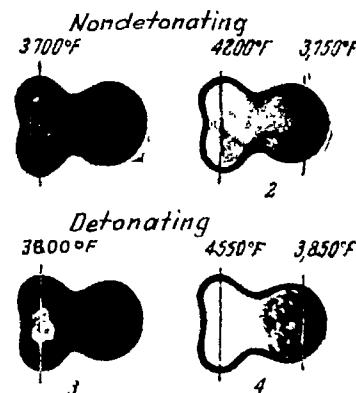


Figure 22.- Temperature at various parts of the charge for normal and detonating combustion in the engine (Withrow and Rassweiler)

1. 10° after ignition,
2. 45° after ignition,
3. 10° after ignition,
4. 35° after ignition.

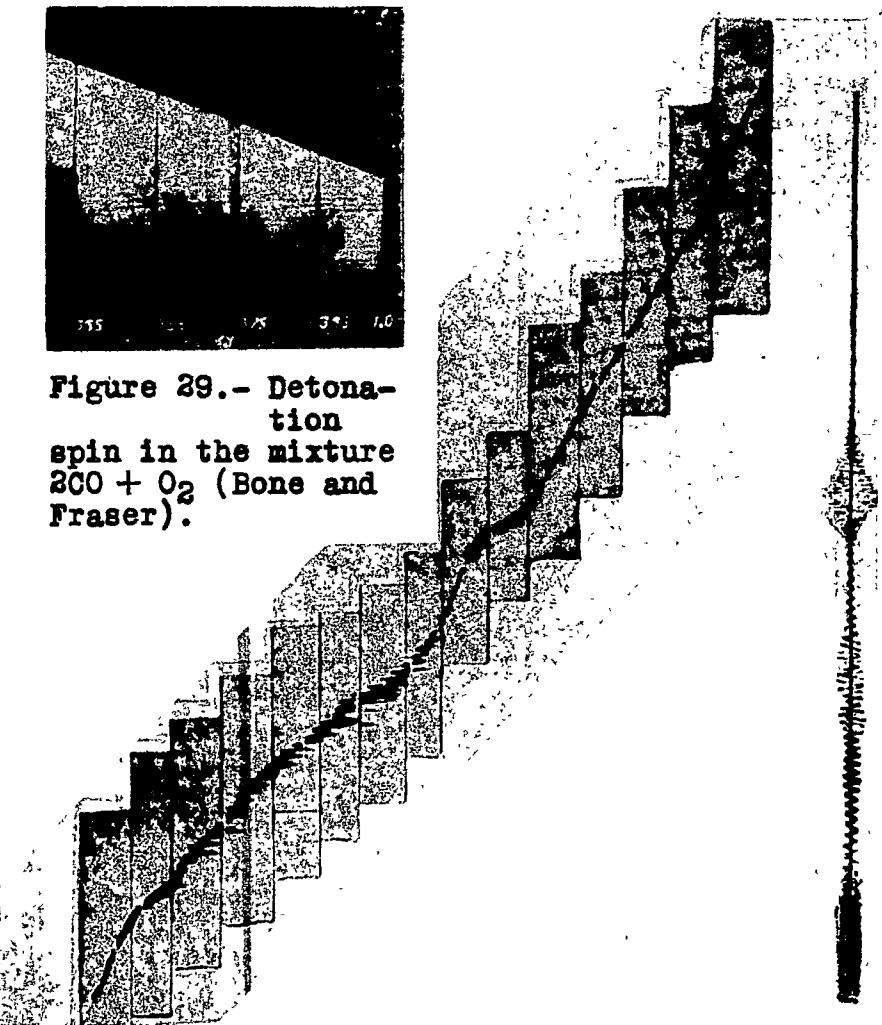


Figure 23.- Photographs of vibrational combustion with the pressure diagram for the combustion of methane in an open tube (Coward and Hartwell).

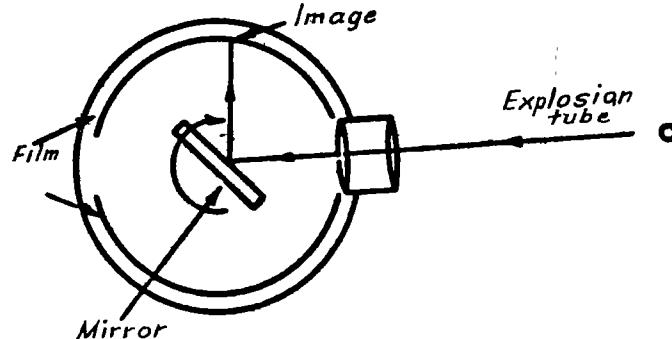


Figure 27.- High-speed mirror arrangement of Fraser camera.

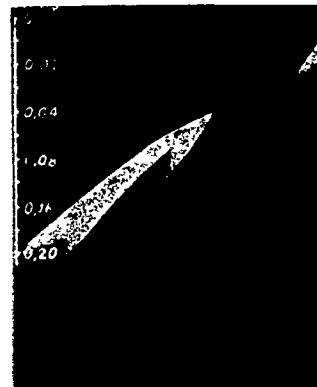


Figure 28.- Photograph of explosion wave in the mixture $\text{CO}_2 + \text{O}_2$ (Bone, Fraser and Wheeler).

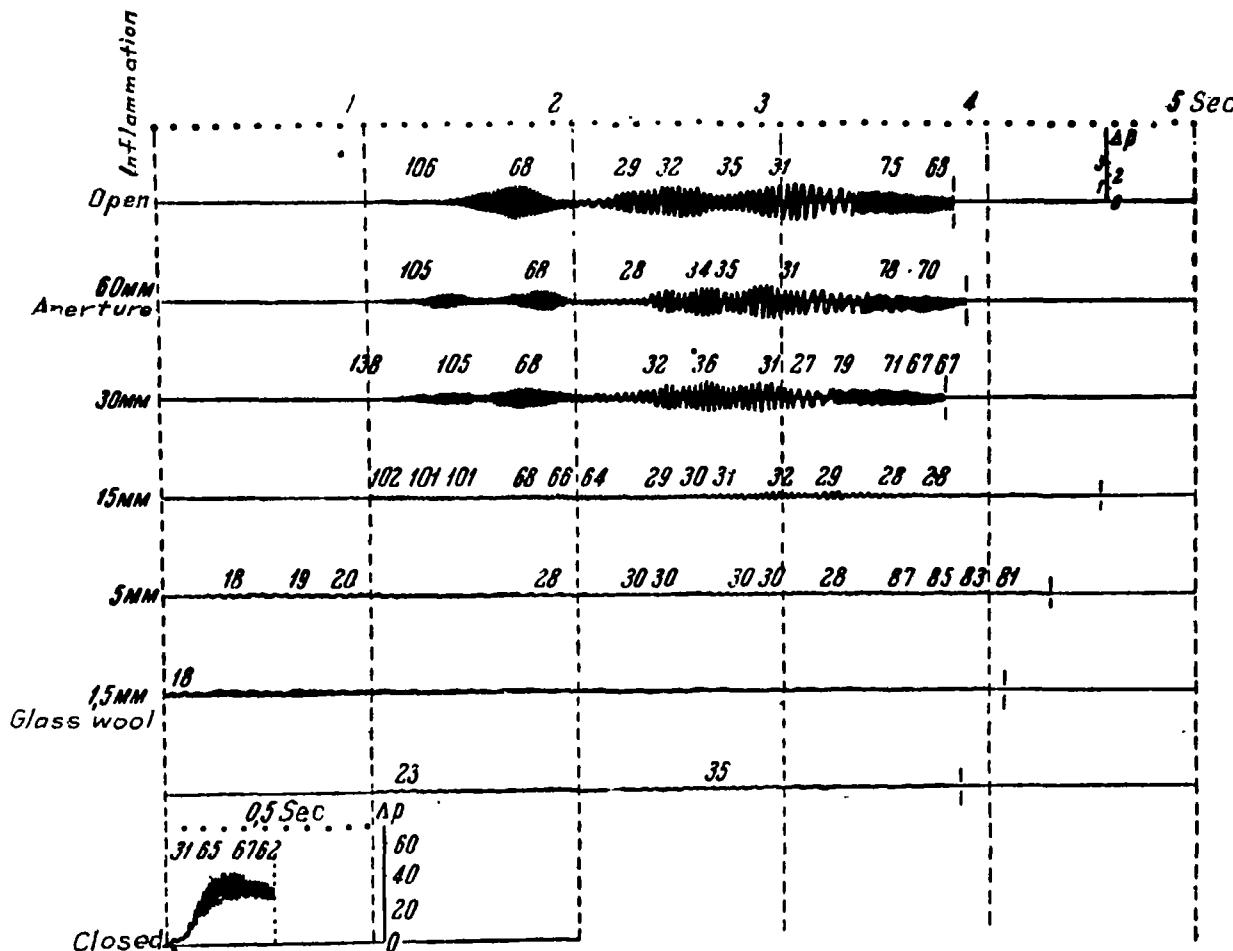


Figure 24.- Variation of the amplitude of vibration of the pressure for various degrees of opening of the tube (Coward and Hartwell). ΔP change in pressure in pounds per square inch.



Figure 30.- Detonation spin in the mixture $2\text{CO} + \text{O}_2$ obtained at high speed (Bone, Fraser and Wheeler).

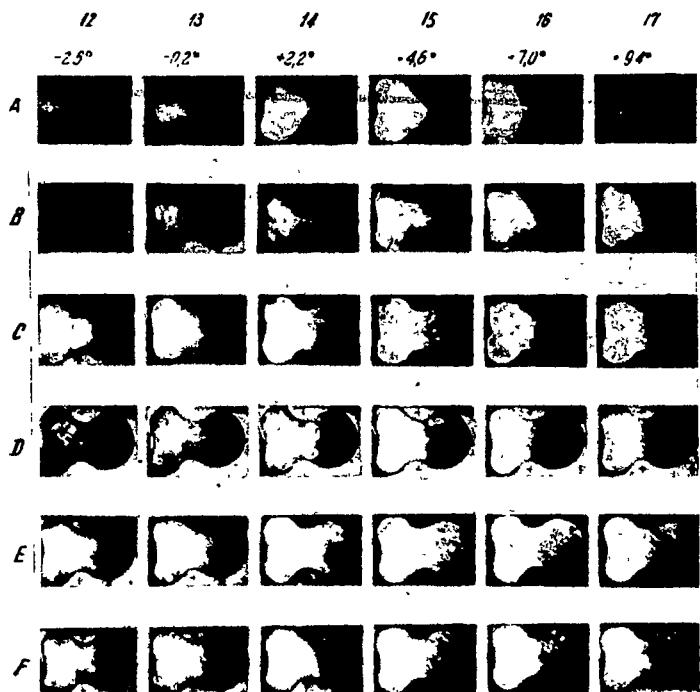


Figure 31.- Series of instantaneous photographs of detonating combustion in the engine (Winthrop and Rassweiler).

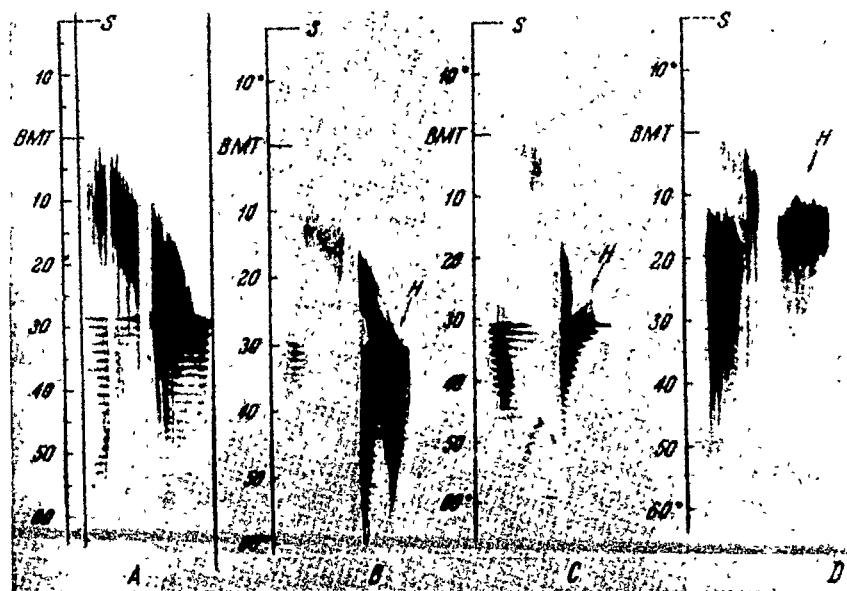


Figure 32.- Record of detonating combustion in the engine (Sokolik and Voynov).
H - self-ignition ahead of the primary flame front.

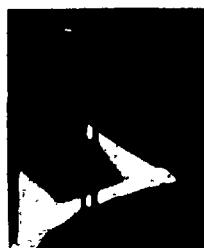


Figure 33.— Record of flame "ejection" in a mixture of butane and oxygen (Laffitte).

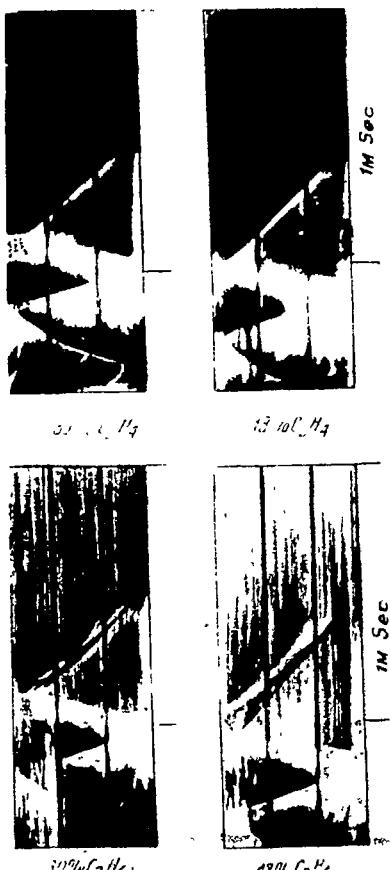


Figure 35.— Recording of flame (upper picture) and shock wave (lower picture) during the formation of a detonation wave in mixtures of ethylene with oxygen (Payman and Titman).

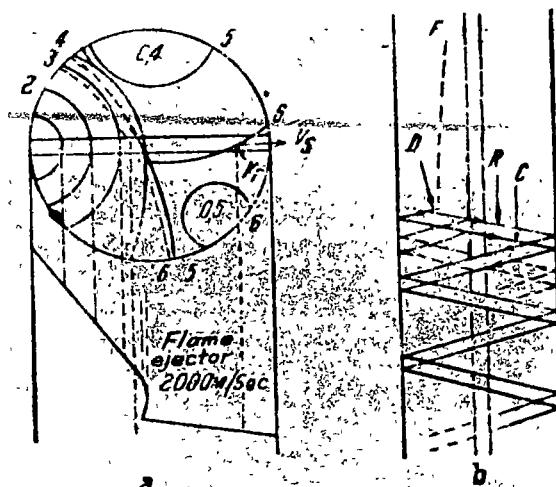


Figure 34.— a, possible explanation of Sokolik and Voynov, side centers of inflammation; b, scheme of high speed photograph record of detonation wave in the engine (Sokolik and Voynov).
F, primary flame front;
D, detonation wave;
R, retonation wave;
C, reflected shock wave.



Figure 36.— Antidetonating combustion chamber (Serruys).

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